

**GAS-PHASE MERCURY OXIDATION: EFFECTS OF BROMINE, CHLORINE
AND SO₂ UNDER AIR FIRING AND OXY-FUEL CONDITIONS,
EXPERIMENTAL AND MODELING STUDY**

by

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ABSTRACT

The mercury in coal is emitted in its elemental state when the coal is burned. As the combustion flue gas cools, reactions under homogeneous and heterogeneous conditions between mercury and species such as chlorine, bromine, SO_x and NO_x can take place. The temperature and concentration of these species determines the extent of mercury oxidation.

The main objective of this study was to evaluate the effects of bromine, chlorine, SO_x and NO_x on gas-phase mercury oxidation reactions in flue gas. This study used a methane-fired, bench-scale reactor and CHEMKIN software for performing kinetic calculations. The model included reaction pathways to account for halogen, mercury, and combustion chemistry.

The experimental results showed that chlorine is not effective as a gas-phase oxidant of mercury compared with other halogens such as bromine. In presence of bromine, a significant extent of mercury oxidation was observed at the two quench rates evaluated in this study. Extents of oxidation in the presence of bromine decreased when SO_2 was present.

A wet conditioning system was used to determine mercury speciation in oxidized and elemental species. The total side of the system reduces oxidized mercury back to elemental using a stannous chloride-hydrochloric acid solution. The elemental side contains a solution of potassium chloride-sodium thiosulfate which retains oxidized

species and does not interact with the elemental mercury species. A solution of sodium hydroxide was installed in both sides of the conditioning system to remove acid species before they reach the mercury analyzer. The solutions on both sides of the conditioning system, the total and the elemental, were modified to decrease biases in measurements when working with bromine.

Replacing the combustion air with a mixture of 27%O₂ in CO₂ caused a large increase in the apparent extent of oxidation by chlorine, increasing it from 2% to 70% at 100 ppm Cl (as HCl). Oxygen firing had little impact on oxidation by bromine. The presence of 500 ppm SO₂ caused a dramatic decrease in oxidation, particularly for chlorine.

*A mi esposo Andrés, mis padres Mercedes y Raúl, mi hermana Viviana,
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NOMENCLATURE

A	Pre-exponential factor in the Arrhenius equation
$\mu\text{g}/\text{m}^3$:	Micrograms per cubic meter
$^{\circ}\text{C}$:	Degrees Celsius
Br:	Atomic Bromine
Br ₂ :	Molecular Bromine
BrCl:	Bromine Monochloride
cm:	Centimeters
CaBr ₂ :	Calcium Bromide
Cl:	Atomic Chlorine
Cl ₂ :	Molecular Chlorine
CO:	Carbon Monoxide
CO ₂ :	Carbon Dioxide
E _a	Activation Energy
H ₂ O:	Water
HBr:	Hydrogen Bromide
HCl:	Hydrogen Chloride
Hg ⁰ :	Elemental Mercury
Hg ⁺ , Hg ²⁺ :	Oxidized Mercury Species
Hg ^p :	Particulate-bound Mercury

HgBr ₂ :	Mercury (II) Bromide
HgCl:	Mercury (I) Chlorine
HgCl ₂ :	Mercury (II) Chlorine
HQ:	High Quench
ID:	Inner Diameter
k	Reaction Constant
K:	Kelvin
KBH ₄ :	Potassium Borohydride
KCl:	Potassium Chloride
K/s:	Kelvin per Second
L/min:	Liters per Minute
LQ:	Low Quench
M	Molar Concentration
MFC:	Mass Flow Controller
ml/min:	Milliliters per Minute
n	Unitless Power
N ₂ :	Nitrogen
Na ₂ S ₂ O ₃ :	Sodium Thiosulfate
NaOH:	Sodium Hydroxide
NH ₂ OH-HCl:	Hydroxylamine - Hydrochloride
NO:	Nitrogen Monoxide
NO _x :	Nitrogen Oxides
NO ₂ :	Nitrogen Dioxide

O ₂ :	Oxygen
OCl ⁻ :	Hypochlorite Ion
OD:	Outer Diameter
ppm:	Parts per Million by Volume
pptv:	Parts per Trillion by Volume
slpm:	Standard Liters per Minute
R	Ideal Gas Constant
SnCl ₂ :	Stannous Chloride
SO _x :	Sulfur Oxides
T	Temperature
THAM/EDTA:	Tris-hydroxymethyl aminomethane/Ethylenediaminetetraacetic Acid
SO ₂ :	Sulfur Dioxide
Vol.:	Volume
W:	Watts
wt:	Weight

LIST OF ABBREVIATIONS

CEM	Continuous Emissions Monitor (CEM)
CSTR	Completely Stirred Tank Reactor
EPA	Environmental Protection Agency
ESP:	Electrostatic Precipitator
FGD:	Flue Gas Desulphurization
GRI	Gas Research Institute
HWC	Hazardous Waste Combustor
MFC	Mass Flow Controller
NEMS	National Energy Modeling System
OH	Ontario Hydro
PBR	Packed Bed Reactor
PFR	Plug-Flow Reactor
REI	Reaction Engineering International
SCEM	Semi-Continuous Emission Monitor
SCR:	Selective Catalytic Reduction
SRI	Southern Research Institute

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CHAPTER 1

INTRODUCTION AND BACKGROUND

Mercury is a hazardous pollutant for both humans and the environment. The Environmental Protection Agency (EPA) has classified it as a hazardous material and its emission from different sources is regulated (1).

One of the major sources of atmospheric mercury is the flue gas derived from the combustion of fossil fuels such as coal. In 2008, 48 % of the electricity generated in the US came from coal (2). Mercury is an impurity in coal that is emitted to the atmosphere when it is burned; the mercury content as well as the amount of mercury emitted varies with the type of coal. According to the National Energy Modeling System (NEMS), the average mercury content of coal ranges from 2.04 pounds per trillion Btu for low-sulfur, subbituminous originating from mines in the Rocky Mountain region to 63.90 pounds of mercury per trillion Btu for waste coal (2).

The speciation of mercury in its three states, elemental (Hg^0), oxidized (Hg^{2+}) and particulate bound (Hg^p), depends on the concentration of sulfur and halogens in the coal, flue gas temperature and composition. The speciation affects choices for emission control. The oxidized (Hg^{2+}) can be collected by devices such as flue gas desulfurization (FGD) scrubbers, and particulate bound (Hg^p) forms are generally trapped by existing pollutant and particulate control devices such as electrostatic precipitators (ESP) and fabric filters, as shown in the sketch of a typical power plant configuration in Figure 1.1.

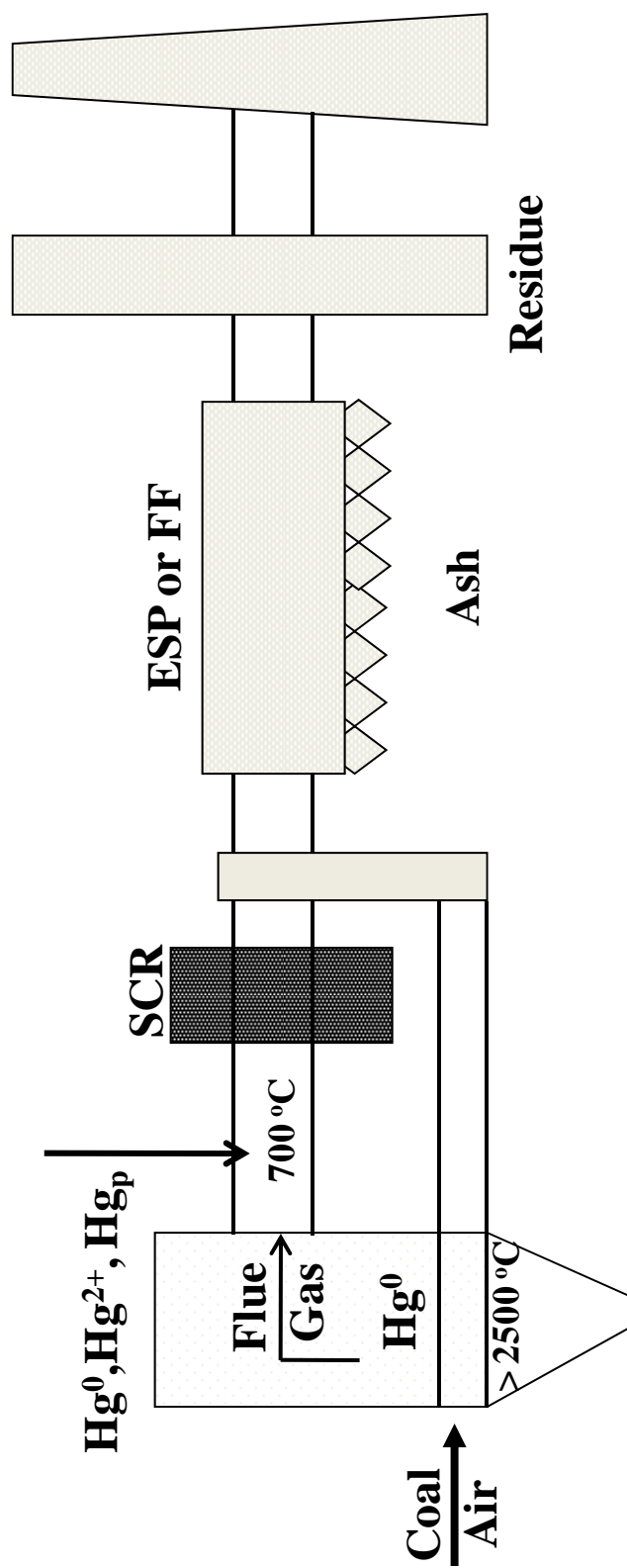


Figure 1.1. Typical power plant configuration with air pollution control devices. Adapted (3)

In contrast, elemental mercury is only slightly soluble in water and is highly volatile at typical combustion and air pollution control temperatures which make its capture by conventional means difficult. Elemental mercury emitted to the atmosphere enters the food chain via the process shown in Figure 1.2.

Methods that enhance the transformation of elemental mercury to its oxidized or particulate bound forms are crucial for controlling emissions. Previous studies have determined that typical flue gas components such as chlorine, SO₂ and bromine play a major role in the extent of mercury oxidation in coal combustion systems (5-9). Recently, the injection of bromine has been shown to be an effective way of increasing oxidation (10, 11). However, data and kinetics on the interactions between mercury and bromine are limited because of difficulty of making mercury measurements, particularly in the presence of bromine.

The extent of mercury adsorption by the fly ash has also been studied and found to be affected by surface functional groups on carbon, surface area, and temperature among others (12-14). In addition, commercial activated carbons have been developed to increase the efficiency of the adsorption and oxidation (15, 16).

Recent studies have also focused on greenhouse gas emissions (17-19). Among all gases, emissions of CO₂ are by far the most significant contributor to green house gases. Several measures have been proposed to reduce CO₂ emissions. Sequestration of CO₂ is one. The O₂/CO₂ (oxy-fuel) combustion process results in a concentrated CO₂ stream that helps reduce the cost of sequestration. In this process, the fuel is burned with a mixture of oxygen and recycled flue gas yielding a high CO₂ concentration in the product flue gas, thereby lowering the capture cost. The high CO₂ composition of the flue gas could affect

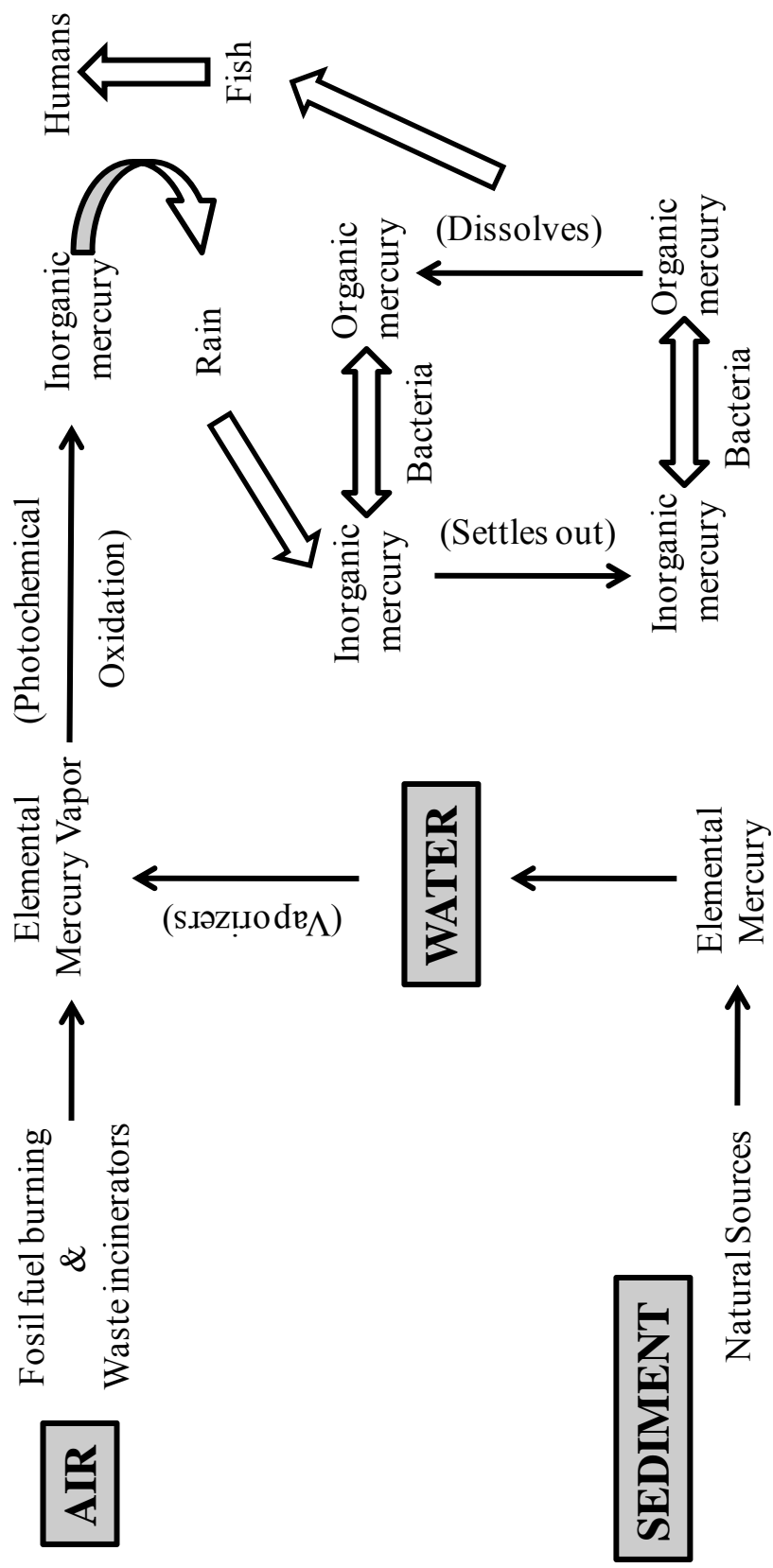


Figure 1.2. Mercury atmospheric cycle. Adapted (4)

the mercury transformation processes occurring in flue gases. The effects of oxy-firing on mercury oxidation are not well characterized.

Literature Review

Mercury Transformations in Coal- Combustion systems

The effectiveness of mercury capture technologies is dependent on mercury speciation and flue gas composition. The design and application of diverse emission control techniques is facilitated by a detailed understanding of the kinetic and thermodynamic behavior of mercury at the different temperatures regimes. This kinetic information is also helpful for the development of mercury-halogen mechanisms to predict the extents of oxidation that would be attained in different environments.

The concentrations of the three main forms of mercury in coal-combustion systems, elemental Hg^0 , particulate Hg^{P} and oxidized Hg^+ , Hg^{2+} , are determined, in part, by coal properties and the resulting concentrations of species such as Cl , Cl_2 , and HCl . The concentration of mercury in coal is on the order of 0.1 ppm; this mercury is vaporized in the combustion zone resulting in elemental mercury concentrations in the range from 1 to 20 $\mu\text{g}/\text{m}^3$ (20). It is expected that mercury will remain in its elemental state, its thermodynamically favored form, at the exit of the furnace (1700K). As the combustion gases cool, gas phase reactions and heterogeneous interactions result in oxidized and particulate-bound forms, respectively. At lower temperatures (about 950K) the formation of species such as HgCl_2 starts and continues as the gas cools down until the temperature reaches 700K; at this temperature the formation of HgCl_2 stops at a lower concentration than predicted by the equilibrium calculations, which could be an indication of kinetic limitations in the oxidation of elemental mercury in typical

combustion environments (21). It has also been suggested (21) that 5-95% of the gas phase mercury could be present in the oxidized form Hg^+ in the effluent stream from different boilers.

Mercury speciation is also affected by the air heater and air pollution equipment in the postcombustion region of the boiler. Elemental mercury can be oxidized to HgO and HgCl_2 in the air heater and the electrostatic precipitator (ESP); elemental and oxidized mercury can be adsorbed on the particulate matter present in both devices generating some particulate-bound mercury, Hg^p . In the flue gas desulfurization systems (FGD), elemental and oxidized mercury species can be absorbed into the scrubber solution; the extent of this process is strongly dependant on the speciation of mercury, mass transfer limitations in the scrubber, the liquid-to-gas ratio, and the design of the scrubber (22, 23).

Overall, factors like the type of combustion system, type of coal, temperature and residence time in particulate control devices and air pollution control systems (FGD, SCR) can affect mercury speciation by modifying factors such as chlorine and ash content, unburned carbon in the fly ash, oxidized and particulate mercury concentration in the exhaust gas, among others. Figure 1.3 shows a summary of the possible transformations that mercury can undergo under combustion conditions (24).

Elemental mercury in combustion systems can also react with other flue gas components such as O_2 (g) and NO_2 (g) although kinetic limitations and short residence time represent factors that make these reactions less viable under combustion conditions. However, these species can act as catalysts in the elemental mercury adsorption on carbonaceous materials at low temperatures (100-300⁰C) (25, 26).

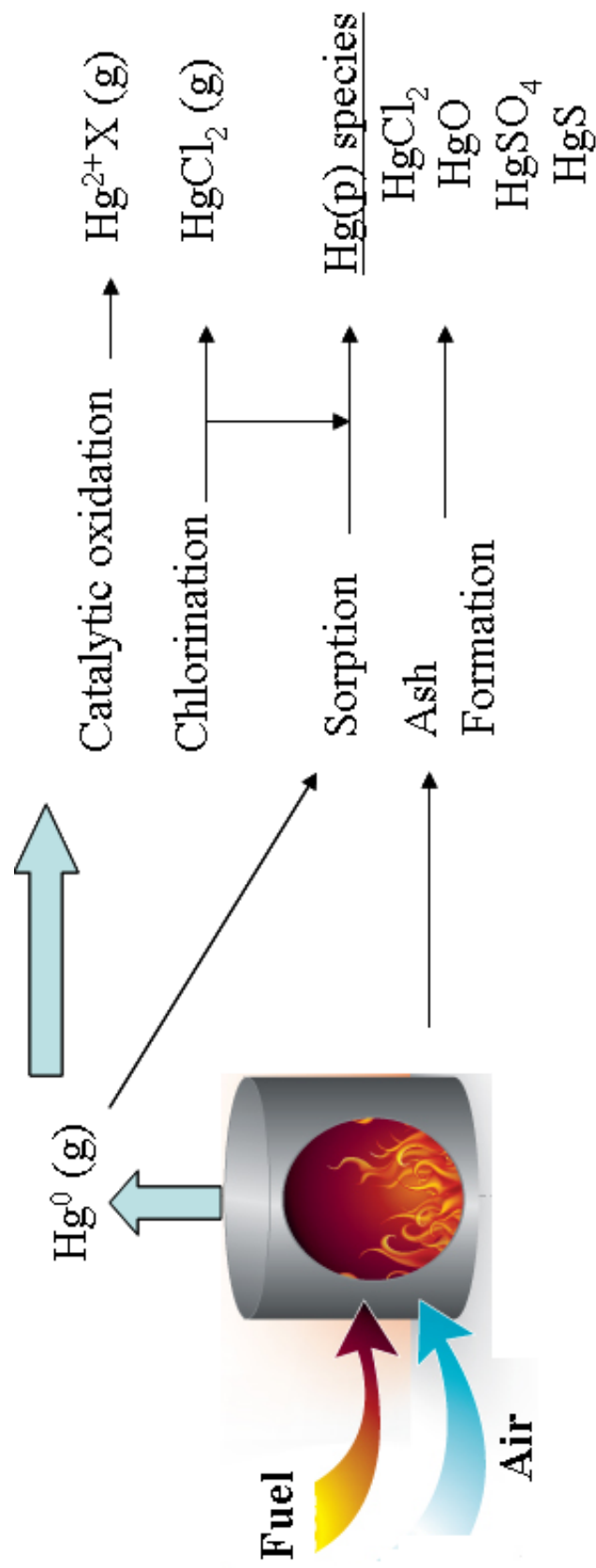


Figure 1.3. Mercury transformation during coal combustion. Adapted (24)
X = halogen.

Specifically, the effect of NO_2 (g) on mercury speciation seems to be very dependent on the temperature. At 175°C , Laudal et al. (27) determined that NO_2 (g) concentrations as low as 20 ppm can have a double effect on mercury speciation, inhibiting the adsorption of elemental mercury but promoting its oxidation, which contradicts the observations by Hall et al. (25,26).

Sulfur dioxide also has potential effects on mercury speciation in both the gas phase and the sulfur-rich ash particles entrained in the flue gas. About 1-3 % of SO_2 (g) is transformed to SO_3 (g), which in turn, is transformed to H_2SO_4 (28). Below its dew point, H_2SO_4 can condense on the surface of carbonaceous particles allowing mercury species absorption (29). The presence of SO_2 can cause the reduction of oxidized mercury species (30,31) due to the consumption of oxidizer species such as chlorine (24).

In addition to the species generated from coal combustion, recent studies have shown that the injection of halogens like bromine to the flue gas could result in higher extents of elemental mercury oxidized compared to those obtained in presence of chlorine. Although most of the thermodynamic and kinetic data available for mercury-bromine reaction is the result of atmospheric studies (32, 33), some studies performed at temperatures typical of combustion systems have determined that for a typical temperature profile along a gas-cleaning system, the oxidation of elemental mercury by bromine to produce HgBr_2 starts as the gas cools down below 700K; the reaction is continuously accelerated until a temperature of 500K is reached. The instability of the HgBr species at temperatures below 500K stops the formation of HgBr_2 (21,34).

As the temperature of the gas decreases when it approaches the air preheater, the HgBr_2 starts to be generated in contrast to the HgCl_2 production which is not favored at

these conditions (21, 34). Both species, HgCl_2 and HgBr_2 , reach steady-state concentrations in the electrostatic precipitator.

Niksa et al. (35) used a model to simulate a reaction system that included the gas-cleaning system from the furnace exit through the FGD outlet including the back-end heat exchangers, SCR, air preheater, electrostatic precipitator, or fabric filter and FGD. This system has a huge temperature drop from a furnace exit gas temperature of about 1050°C to a smokestack inlet temperature of less than 100°C . They determined that at typical postflame conditions, HBr dissociates into the more reactive species in a more efficient way than HCl , facilitating the higher extents of elemental mercury oxidation observed in presence of bromine than in the case of chlorine. This higher oxidation by bromine was also attributed to the fact that the Br atoms are present in similar concentration as HBr at the furnace exit, in contrast to the low concentration of Cl atoms observed under these conditions (35). These observations were in good agreement with the experimental findings presented by Cao et al. (6), who observed a similar behavior for mercury oxidation in the presence of bromine and chlorine species. Further into the gas-cleaning system, a rapid recombination of Br atoms to generate HBr and Br_2 species is observed at the back-end heat exchangers; this recombination results in a plateau of the HBr concentration at 600°C and 160°C for Br_2 species (35).

Based on the observations by Niksa et al. (35) and Senior et al. (20, 21), mercury-chlorine reactions seem to be more favorable at temperatures in the range 700-950K while interactions of mercury-bromine were observed to start around 700-500K. Below 500K most of the reactions affecting mercury speciation appear to be heterogeneous, either adsorption of mercury species or reactions of elemental mercury with species on

the surface of the fly ash. At these lower temperatures, the formation of interhalogen species like BrCl as a result of HCl-HBr interactions can also be observed (6).

In the next sections, an introduction to previous experimental and modeling studies on mercury transformations due to homogeneous and heterogeneous interactions will be presented.

Homogeneous Mercury Oxidation

Under homogeneous conditions, the presence of species such as chlorine, bromine and SO₂ in the flue gas derived from coal combustion systems has a major impact on mercury oxidation by either increasing the extent of oxidation or inhibiting it (3, 6, 8, 10). The following section will show a literature review on the main gas-phase interactions between mercury and some of the flue gas components as well as some of the issues found during the experimental measurements of mercury speciation.

Gas-Phase Mercury Oxidation by Chlorine

As a product of the combustion process, chlorine can be emitted as atomic chlorine that later reacts to form HCl or molecular Cl₂ depending on the oxygen concentration and quench rate (5, 6). Elemental mercury from the coal can react with chlorine species to form oxidized mercury compounds such as HgCl and HgCl₂ (6).

Sliger et al. (7) used a natural gas-fired flow reactor as a source of reactants to study mercury oxidation by chlorine. The gas composition was 7.43 % O₂, 6.15 % CO₂, 12.3 % H₂O, balance N₂, the initial mercury concentration was 53 µg/m³ and the HCl concentration varied from 0 to 500 ppm. A simplified EPA Method 29 was used to measure mercury speciation. According to the authors, this system could suffer from

interferences in the measurement of mercury in the presence of either SO₂ or molecular chlorine. They support the reliability of their measurements by the fact that there is no SO₂ in the system and that the interferences of molecular chlorine become important at concentrations higher than 50 ppm. Based on their kinetic calculations, this level of Cl₂ is never achieved under the conditions of their study. At 200 ppm HCl, the observed mercury oxidation was 70 %. The general trend suggested by the authors was that mercury oxidation increased with increasing the HCl concentration. These experimental observations do not agree with the results obtained by Cauch et al. (36), who determined that at their highest concentration of chlorine (400 ppm, as HCl equivalent), the extent of the oxidation was below 10%. According to Cauch et al. (36), the extent of mercury oxidation by chlorine measured using a wet conditioning system, in which the oxidized mercury species are retained by a KCl solution, could be biased due to the formation of hypochlorite ion in the impinger. Their hypothesis was that the hypochlorite ion oxidized the elemental mercury in the liquid phase thereby increasing the apparent extent of mercury oxidation. The authors showed that the addition of sodium thiosulfate to the KCl impinger prevents this liquid-phase oxidation from occurring. With this new configuration, mercury oxidation by chlorine did not exceed 10 %. For their study, Cauch et al. (36) used a methane-fired quartz reactor to generate the flue gas. The initial mercury concentration was 25 µg/m³ and the quench rate was 440 K/s. Hence, the different oxidation levels observed by Sliger et al. (7) and Cauch et al. (36) could be explained by the absence of sodium thiosulfate on the elemental side of the conditioning system used by Sliger et al. (7). Linak et al. (58) also observed the bias in mercury oxidation measurements in presence of chlorine. In their work, Linak et al. (58) studied

the effect of chlorine on mercury oxidation using two different wet conditioning systems the Ontario Hydro (OH) and the Alkaline Mercury Speciation methods. They observed a bias of about 10-20% in elemental mercury for chlorine concentrations as low as 1 ppm in the simulated flue gas mixture. It was suggested by the authors that this deviation was generated from liquid-phase interactions occurring inside the liquid-phase solutions of the conditioning system rather than gas-phase interactions. It was probable that the hypochlorite ion (OCl^-) in the potassium chloride impinger was oxidizing some of the elemental mercury leading to a false increase in the extent of mercury oxidation. This deviation in mercury measurements was mitigated by the addition of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) to the potassium chloride solution. This component reacts with OCl^- reducing its concentration in the solution and thus decreasing its possibility of oxidizing the elemental mercury.

The absence of sodium thiosulfate may also explain the high oxidation levels reported in other studies like that performed by Laudal et al. (8). In this study, the authors concluded that chlorine (injected as both HCl and Cl_2) had a significant effect on mercury oxidation. The gas composition used was 4% oxygen, 15% carbon dioxide, 10% water vapor, and balance in nitrogen. The initial mercury concentration was $20 \mu\text{g}/\text{m}^3$. For the mercury speciation measurements the authors used different conditioning systems, the Ontario Hydro, the EPA Method 29 and the Mercury Speciation Adsorption (MESA); based on the description provided by the authors. None of these systems have sodium thiosulfate as a component in the impinger solutions. Additional gases were injected: sulfur dioxide 0 to 1500 ppm, hydrogen chloride 0 to 50 ppm, nitrogen oxides NO or NO_2 0 to 600 ppm. The authors determined that the extent of mercury oxidation in presence of

100 ppm Cl_2 was 84.8 % while in the presence of 50 ppm HCl it was just 0.3 %. Even higher are the extents of oxidation reported by Agarwal et al. (9) who found 72 % oxidation with just the addition of 2 ppm chlorine (injected as Cl_2 equivalent). The lab-scale reactor used by the authors included an air preheater, steam preheater, reactor, heat exchanger, mercury generation system (CAVKIT), sorbent injection system (the facility was designed to be able to operate under both homogeneous and heterogeneous conditions), Semicontinuous Emission Monitoring (SCEM) PS Analytical Sir Galahad 10.525 connected to a conditioning system with two impingers, one contains a KCl-NaOH solution, the second one contains a SnCl_2 -NaOH solution. The temperature varied along the reactor from 150 to 538°C and the baseline gas composition consisted of 96.5 % nitrogen, 3.5 % oxygen and 10 $\mu\text{g}/\text{m}^3$ of elemental mercury.

Biased mercury oxidation measurements could also lead to wrong conclusions about the mechanisms of reaction in kinetic studies. Based on their experimental observations, Agarwal et al. (9) determined that the chlorine molecule is a much stronger mercury oxidant than the chlorine atom. This conclusion contradicts others findings (20, 21). Senior et al. (20, 21) showed that the oxidation of mercury by chlorine takes place mainly through a two-step mechanism, the generation of HgCl from the reaction of Hg with Cl and then an additional oxidation of HgCl to HgCl_2 , with the formation of HgCl being the rate controlling step. The conclusions reached by Cao et al. (6) are also in contrast to the mechanism suggested by Senior et al. (20, 21). Cao et al. (6) suggested that the formation of HgCl is fast and not rate controlling and it is the second reaction that controls the rate. The authors performed their tests on 100 MW, front wall-fired

boiler with a cold-side ESP, no SO₂ control, and low-NO_x burners. Mercury speciation measurements were performed using an Ontario Hydro Method and SCEM sampling.

Cao et al. (6) also determined that, although the oxidation process is thermodynamically favorable, it can be kinetically limited under typical combustion conditions. The Cl atoms are the key factor controlling the oxidation process, but factors such as the short lifespan of Cl atoms in the flue gas and the short residence time of the flue gas limit the extent of oxidation.

In general, previous studies have found that chlorine is an important oxidant for mercury. However, apparent oxidation can occur when mercury speciation measurements involve wet conditioning systems.

Effect of the Simultaneous Presence of Chlorine and SO₂ on Mercury Oxidation

The effects of SO₂ on gas-phase oxidation by chlorine are difficult to discern because SO₂ is a dechlorination agent in aqueous solutions. A review of the oxidation literature suggests that the apparent inhibition of oxidation by SO₂ is primarily due to its ability to prevent the aqueous-phase oxidation of elemental mercury.

Cauch et al. (36) showed that the addition of SO₂ had no effect on mercury oxidation by chlorine at SO₂ concentrations below 400 ppm; an increase in mercury oxidation was observed at SO₂ concentrations higher than 400 ppm. The authors used a methane-fired quartz reactor to generate the flue gas presented in Table 1.1. The initial mercury concentration was 25 µg/m³ and the quench rate was 440 K/s. Laudal et al.(8) determined that the addition of 1500 ppm SO₂ to a flue gas containing 4 % oxygen, 15 % carbon dioxide, 10 % water vapor and balance nitrogen resulted in 0.7 % oxidation.

Table 1.1 Flue gas composition for experiments. Adapted (36)

Species	Concentration
O₂	0.8 vol. %
H₂O	16.5 vol %
CO₂	7.7 vol. %
NO	30- 500 ppm
SO₂*	0 - 500 ppm
HCL**	0 - 500 ppm
HBr***	0 - 50 ppm
Hg⁰	25 g/Nm ³

* Bottle composition 6000 ppm (SO₂) in air.

** Assuming all chlorine added as HCL (bottle composition 6000 ppm Cl₂ in air).

*** Assuming all bromine added as HBr (bottle composition 3000 ppm Br₂ in air).

Agarwal et al. (9) studied the effect of SO₂ on mercury oxidation by chlorine using a system consisting of an air preheater, steam preheater, final preheater, reactor and heat exchanger. This system was suitable for working under homogeneous and heterogeneous conditions. The mercury source was a CAVKIT (PS Analytical) and the mercury speciation system included a PS Sir Galahad 10.525 coupled to a wet conditioning system. The baseline gas composition is showed in Table 1.2. They found that the addition of 370 ppm SO₂ generated a decrease in mercury oxidation by chlorine from 70 % to 52.3%. They also observed that the effect of SO₂ on mercury oxidation by chlorine was stronger when water was present in the system. According to Agarwal et al. (9) the inhibitory effect of SO₂ on mercury oxidation by chlorine could be explained by the irreversible reaction between Cl₂ and SO₂ which is slightly favorable at the typical temperatures in the last section of the power plant.



Table 1.2. Summary of components and composition. Adapted (9)

Component	Composition
Nitrogen	0.7
Oxygen	0.035
Carbon Dioxide	0.135
Water	0.13
Sulfur Dioxide	370 ppm
Nitric Oxide	170 ppm
Carbon Monoxide	300 ppm
Chlorine (HCl or Cl ₂)	100 ppm
Elemental Mercury	10 mg/m ³

An important reduction in oxidation by chlorine in presence of SO₂ was also observed by Sterling et al. (37). They studied the effect of SO₂ and NO on mercury oxidation by chlorine. A methane-fired bench-scale system was used. The mercury speciation was measured by a Semtech Cold Vapor atomic adsorption spectroscopy based continuous mercury analyzer. The authors founded that the extent of mercury oxidation by chlorine is strongly reduced in the presence of SO₂. The observed mercury oxidation by 500 ppm chlorine was about 90% which was reduced to 40 % in the presence of 400 ppm SO₂.

It is very important to notice that the extents of oxidation by chlorine reported by Argawal et al. (9) and Sterling et al. (37) were very high compared to the experimental findings of Cauch et al. (36) (10 % mercury oxidation in presence of 400 ppm chlorine). These results suggest a bias in the measurements performed by Argawal et al. (9) and Sterling et al. (37) due to the impinger chemistry interactions generated from the chlorine present in the system and the lack of sodium thiosulfate in the wet conditioning system .

The 2002 EPA report (38), which was focused on the control of mercury emissions, determined that the gas phase mercury oxidation by Cl is kinetically limited

and inhibited by the presence of SO_2 and water vapor. For the EPA study the simulated flue gas contained 40 ppm of elemental mercury, 5 mole % CO_2 , 2 mole % O_2 , and balance nitrogen, HCl was added in concentrations from 50 to 200 ppm, 500 ppm SO_2 and 1.7 mole % of water were also added. The temperature of the simulated flue gas was 754°C . It was observed that the mercury oxidation by 200 ppm chlorine decreased from 25 % to 15 % in presence of 500 ppm SO_2 .

Laudal et al. (8) studied the effect of some flue gas components such as HCl, SO_2 and NO_x on mercury oxidation at 175°C . They performed some bench-scale tests in which the gases were delivered through mass flow controllers, the mercury was fed from a permeation tube and the mercury speciation was measured by different methods. The authors concluded that for the conditions of their study, the best option for mercury speciation was the Ontario Hydro Method. The baseline gas composition is shown in Table 1.3. Laudal et al. (8) determined that the extent of mercury oxidation decreased from 84.8% in presence of 10 ppm Cl_2 to 1.9 % in presence of 10 ppm Cl_2 , 1500 ppm SO_2 and 50 ppm HCl. The observed extent of mercury oxidation in the presence of 50 ppm of HCl (without Cl_2 or SO_2) was 0.3%. This study offers an important insight on the different extents of oxidation that may be obtained in the presence of just HCl compared to the case of a combination HCl- Cl_2 ; the oxidation obtained with HCl alone is more comparable to the unbiased measurements observed by Cauch et al (36).

Overall, previous studies showed an inhibitory effect of the SO_2 on mercury oxidation by chlorine. Although these studies explained their results on the basis of gas phase interactions, care should be taken regarding possible liquid phase reactions inside the impingers on wet conditioning systems.

Table 1.3 Gas composition for bench-scale tests (wet basis). Adapted (8)

Gases	Nominal Concentration
Main	
Oxygen	4%
Carbon Dioxide	15%
Water Vapor	10%
Nitrogen	Balance
Variable	
Sulfur Dioxide	0 or 1500 ppm
Hydrogen Chloride	0 or 50 ppm
Nitrogen Oxides (NO/NO ₂)	0 or 600/30 ppm
Chlorine	0 or 10 ppm
Elemental Mercury	20 µg/Nm ³
HgCl ₂	20 µg/Nm ³

Mercury Oxidation by Bromine

The effect of bromine on mercury oxidation has not been widely studied; just a few studies have shown its effect on mercury oxidation under simulated or full-scale combustion conditions (10, 11). Most of the models and experimental studies have been performed under low temperature, atmospheric conditions (38-45).

Vosteen et al. (11) studied the effect of bromine injection on mercury removal at the Hazardous Waste Combustor (HWC) KILN A of BAYER Industry Services. Bromine was added by co-combustion of bromine-rich and chlorine-rich wastes (normal conditions of the HWC) or by injection of aqueous NaBr or diluted HBr. By injecting Br/Hg ratios higher than 300 all mercury in the boiler exit was converted to its oxidized

form. The authors also suggested that bromine could be a more effective oxidant for mercury than chlorine, due to the predominance of Br_2 rather than HBr and the consumption of the available molecular chlorine by SO_2 at typical combustion temperatures.

It should be noted that in order to get stable oxidation measurements in the presence of bromine, it is necessary to modify the configuration of the wet conditioning systems to avoid biased measurements (46). Although the accumulation of bromine on the stainless steel or glass walls has been cited as potential source of bias in mercury measurements (47), there is no reference to the potential effect of liquid phase interactions on the accuracy of the measurements.

The significant impact of bromine on mercury oxidation has also been observed in other experimental and modeling studies. Although the conditioning systems used in these publications is not completely clear, some ideas that could explain the mercury-bromine interactions in combustion systems are suggested.

Cao et al. (48) studied the effect of the addition of hydrogen halides on the oxidation of elemental mercury generated from the burning of a subbituminous coal. This study was performed with and without the addition of two commercially available selective catalytic reduction (SCR) catalysts. The slipstream reactor used for this study was designed to simulate full-scale applications of a SCR system and air preheater in utility boilers. The average temperature inside the SCR reactor was about 330°C . The mercury continuous emissions monitor (CEM) as well as the Ontario Hydro (OH) Method was used for observing mercury variations during testing. In the absence of SCR catalyst, the addition of HBr showed a strong impact in increasing the elemental mercury

oxidation (~30%). The addition of 3 and 6 ppm HBr resulted in an increase in mercury oxidation from 30% to 83 and 85.9 %. Cao et al. (48) suggested that the impact of different halogens on elemental mercury oxidation followed an inverse atom sequence in the periodic table. Also, according to their results, the authors determined that mercury oxidation through halogen molecules was in general more kinetically favored than through hydrogen halogens.

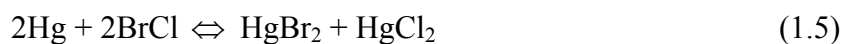
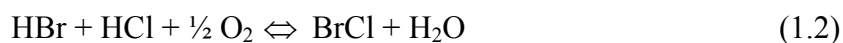
A second study by Cao et al. (49) supports their previous findings about the significant impact of bromine on mercury oxidation. An experimental and thermodynamic study was made about the products and their equilibrium concentrations resulting from the addition of HBr to a typical flue gas composition generated from the burning of two different coals: a bituminous coal and a Powder River Basin coal (PRB). The experimental setup was the same as in the previous study (48). The average flue gas composition was 80 % N₂, 7 % H₂O, 6 % O₂, 13 % CO₂, 300 ppm NO, 1000 ppm SO₂, HCl varied from 80 to 150 ppm, HBr was added in the range between 3 and 30 ppm and the mercury concentration was 10 ppb. The thermodynamic calculations were performed using the F*A*C*T software and the JANAF Thermo chemical tables. For the bituminous coal-fired flue gas with medium sulfur and high chlorine contents, the authors found that after the HBr addition, HgBr₂ forms at a temperature range between 300 and 700°C. The addition of 3 ppm HBr represented a maximum HgBr₂ concentration in the flue gas of 5 % at 550°C but increasing the HBr concentration to 30 ppm increased the HgBr₂ concentration up to 60%. For the flue gas obtained from burning the PRB coal with low sulfur and chlorine contents, the HgBr₂ appeared in a range of temperature between 200-800°C. With the addition of 3 ppm HBr the concentration of HgBr₂ relative

to the total mercury in the flue gas was 80 % at 500°C. At the same temperature, the increase of the HBr addition to 30 ppm caused mercury oxidation (HgBr_2) as high as 100%. Cao et al. (48) concluded that for the two typical flue gas compositions used in the study, the bromine addition resulted in enhanced mercury oxidation.

As cited by all these previous studies, bromine has a higher potential as mercury oxidant than chlorine. One of the proposed theories to explain this behavior was suggested by Liu et al. (52). They studied the oxidation rates of elemental mercury oxidation by Br_2 under flue gas conditions found downstream from the air preheater and upstream from the particulate collectors. The elemental mercury concentration as a function of time was measured by a cold vapor atomic absorption spectrophotometer (CVAAS). The kinetics of the reactions was studied using Pyrex flasks and the absolute rate technique under pseudo-first order conditions. The range of mercury concentrations used in this study varied from 0.01 ppm to 0.20 ppm, the bromine additions varied from 4 to 60 ppm. The temperature was 363K. Liu et al. (52) concluded that the reaction rate for the oxidation of mercury by bromine is more than two orders of magnitude higher than by Cl_2 . They explained this on the basis of a stronger Van der Waals interaction between mercury and Br_2 than between mercury and Cl_2 , suggesting that the bromine is a more effective mercury oxidant compared to chlorine. Bromine interactions with other flue gas components such as NO_x and SO_2 were slower than the reaction between mercury and bromine, making all the Br_2 available for the reaction with mercury. And the higher number of electrons in the bromine molecule compared to chlorine can also increase Van der Waal interactions.

Mercury Oxidation by Bromine and Chlorine

The simultaneous presence of bromine and chlorine can also have an effect on the extent of mercury oxidation due to interhalogen species interactions with elemental mercury. Cao et al. (48,49) suggested a mechanism to explain the formation of these interhalogen species and their effect on mercury oxidation. This mechanism consisted of two interhalogen formation reactions, 1.2 and 1.3, a depletion step (reaction 1.4) and the mercury oxidation by the interhalogen species (reaction 1.5).



Based on experimental mercury oxidation rates that were higher than the ones predicted by their kinetic model, they suggested that bromine could improve the kinetics of mercury oxidation by promoting the formation of activated chlorine.

The equilibrium and kinetics of the reaction between bromine and chlorine to form bromine monochloride (BrCl) was studied by Qu et al. (51). The authors suggested a reaction mechanism and determined the reaction rate for the production of BrCl at 373 K as $2.3 \times 10^{-17} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$. They also determined that the major oxidized species in the flue gas in the presence of both bromine and chlorine was HgCl_2 instead of HgBr_2 which suggested that the bromine acted as an accelerant of the mercury oxidation by promoting the formation of intermediates that react with chlorine to form HgCl_2 . In the

presence of 100 ppm BrCl, the extent of mercury oxidation was more than 90 %. Complete mercury oxidation was observed by the authors in presence of 10 ppm Cl₂ while for 10 ppm Br₂ the oxidation reached 90 %. These observations are in good agreement with the results obtained by Cao et al. (48, 49) regarding the extent of oxidation in presence of bromine and chlorine.

Although the simultaneous presence of bromine and chlorine reduces the amount of bromine required to obtain high mercury oxidation, thereby reducing the accumulation of bromine on the surfaces and the bias in the mercury measurements by wet conditioning systems, there are just a few publications focused on interactions between mercury, bromine, and chlorine.

Mercury Oxidation by Bromine and SO₂

Although SO₂ alone does not seem to have any effect on the extent of mercury oxidation, it can have an important influence on impinger chemistry that can lead to biased measurements. It was difficult to find previous publications about the SO₂ effect on the oxidation by bromine, the only study found in the literature by the author of this dissertation was the one performed by Liu et al. (52). They investigated the effect of typical flue gas components such as SO₂, NO, HCl and H₂O on elemental mercury oxidation by bromine. Under the temperature conditions of their study (T = 276-365K), oxidation did not suffer any detectable change when SO₂ was present at concentrations between 0 and 1300 ppm.

Effects of Bromine on Experimental Measurements of Mercury Species

The studies cited in the previous section have shown that the presence of bromine compounds highly promoted mercury oxidation under homogeneous conditions yet it is important to assure the stability and reproducibility in both total and elemental mercury measurements to clearly determine the extent of oxidation. In this section, we are going to examine previous publications to study some of the problems associated with mercury injections in combustion systems as well as potential solutions.

Berry et al. (53) studied the effect of calcium bromide injection on mercury oxidation at Plant Miller Unit 4. This unit is equipped with a cold side electrostatic precipitator and two SCR catalyst chambers which are designed to operate at 720°F. They observed a negative bias of 15%-40% in the measurement of total mercury concentration by the SCEM with the Ontario Hydro method. It was also found that this bias increased when reactive surfaces such as stainless steel and glass were present in the system. To solve this issue the authors replaced the Ontario Hydro method by the sorbent tube method, eliminated the contact of the flue gas with stainless steel surfaces, and replaced the glass in the impingers by quartz.

Wang et al. (41) studied the kinetics and mechanisms of aqueous elemental mercury oxidation by aqueous bromine species under atmospheric conditions. They used a modified dithizone method to measure oxidized mercury species. The authors found that bromine affected the partitioning of mercury between the aqueous and the organic phase which strongly affected the accuracy of the method for the determination of oxidized mercury species. They also realized that bromine is a strong complexing ligand with divalent mercury making it necessary to account for this effect in the final oxidized

mercury concentration measurements. As a method of solution they used a pH neutral dithizone solution to avoid the formation of the complexing agent and added some sulfite to remove the excess of oxidant inside the solution. This study is a good source of experimental results; however the dithizone method is not a common speciation method. Therefore it becomes difficult to compare the results of this methodology with other studies.

Cao et al. (49) studied mercury transformations in the presence of bromine in a typical flue gas generated from the burning of bituminous or Powder River Basin coals. The reaction system used in this study was designed to simulate full-scale air preheaters and applications of SCR in utility boilers. The authors used an inertial sample probe coupled to an Ontario Hydro method and CEM for mercury measurements. Cao et al. (49) observed an unexpected decrease in the total mercury concentration in the presence of bromine that they attributed to cold spots along the heated sampling probe that caused oxidized species accumulation in the sampling system. They cited the purging and cleaning of the sample probe as the solution to eliminate the bias.

Liu et al. (52) evaluated mercury oxidation rates by bromine using Pyrex flasks and measuring the mercury concentration as a function of time by cold vapor atomic absorption spectrophotometry (CVAAS). The mercury concentration varied from 0.01 ppm to 0.20 ppm while the bromine was added from 4 to 60 ppm. The elemental mercury was excited from the ground state to excited states by exposing it to UV light. The authors found that the Pyrex wall was promoting mercury oxidation by bromine; their approach to eliminate the wall interference was to coat the wall surface with halocarbon wax.

Babi et al. (46) investigated the interferences in continuous flow techniques for mercury measurements in the presence of iodine or bromine. For mercury measurements they used a Tekran Series 2600 CVAFS Mercury system configured in accordance with USA EPA Method 1631. This sampling method included a SnCl_2 -HCl solution as a reduction agent for the oxidized mercury species followed by a NaOH solution. At a mercury concentration of 5 ng/L and in presence of BrCl, the percent of mercury recovery was zero. Babi et al. (46) tested different methods to correct the bromine or iodine interferences: (1) increasing the reaction time between the sample and the SnCl_2 solution which means extending the time available for the reduction reaction between the sample and the SnCl_2 to occur; (2) pH adjustments of the SnCl_2 solution to destroy the Hg-Br and Hg-I complexes; (3) increasing the SnCl_2 solution concentration; (4) replacing the SnCl_2 solution by a potassium borohydride (KBH_4) solution. From all the approaches tested, the authors concluded that the online pH adjustment to levels greater than 9 was the most successful method for correcting the observed interference in mercury measurements. The KBH_4 solution is also a good solution for the mercury bias but more tests are needed to confirm its stability.

Effects of Bromine and SO_2 on Experimental Measurements of Mercury Species

The simultaneous presence of bromine and SO_2 can affect the performance of wet conditioning systems to measure mercury species. This effect can be detected by a bias in the experimental measurements of elemental mercury, and the bias has been associated to the liquid phase oxidation of mercury by bromine species, as cited by Wang et al. (41). In addition, it has been suggested (54-57) that the presence of SO_2 species can influence the

bromine speciation in solution therefore affecting the concentration of the bromine species available to oxidize the mercury.

Liquid Phase Mercury Oxidation by Bromine

Wang et al. (41) investigated the kinetics and mechanisms of the aqueous phase oxidation of elemental mercury by bromine. The Teflon reactor used for this study was kept at 294-296K. Dissolved elemental mercury was allowed to react with bromine in excess at concentrations between 1.125 mM and 2.25 mM at pH in a range of 2-12. Oxidized mercury measurements were carried out using the modified dithizone method. The authors found that bromine speciation and subsequently mercury oxidation depends upon the pH of the aqueous solution (see Table 1.4), and determined the pseudo-first-order rate constants for the reaction between mercury and the different bromine species as summarized in Table 1.5.

They concluded that compared to gas-phase bromine species, the effect of aqueous bromine on the elemental mercury oxidation in the Arctic and sub-Arctic regions is negligible.

Xie et al. (39) presented a model that describes the interactions between mercury and bromine species in both gas and liquid phase under atmospheric conditions. The study was developed using the atmospheric chemistry box model MECCA. The authors worked with the aqueous phase chemistry shown in Table 1.6

Aqueous oxidized mercury can form different complexes with different ligands that could have an important effect on the liquid phase kinetics. The formation of these complexes is treated as chemical equilibrium because oxidized mercury has a high

Table 1.4 Effect of pH on mercury oxidation. Adapted (41)

pH	Reactions
2	$\text{Br}_2(\text{aq}) + \text{Hg}(0) = 2\text{Br}^- + \text{Hg}^{2+}$
	$[\text{Br}_2(\text{aq})] = 1.125 \text{ mM}, E = 0.43 \text{ V}$
	$[\text{Br}_2(\text{aq})] = 2.25 \text{ mM}, E = 0.40 \text{ V}$
7	$\text{HOBr} + \text{H}^+ + \text{Hg}(0) = \text{Br}^- + \text{H}_2\text{O} + \text{Hg}^{2+}$
	$[\text{HOBr}] = 1.125 \text{ mM}, E = 0.696 \text{ V}$
	$[\text{HOBr}] = 2.25 \text{ mM}, E = 0.678 \text{ V}$
12	$\text{OBr}^- + \text{H}_2\text{O} + \text{Hg}(0) = \text{Br}^- + 2\text{OH}^- + \text{Hg}^{2+}$
	$[\text{HOBr}] = 1.125 \text{ mM}, E = 0.079 \text{ V}$
	$[\text{HOBr}] = 2.25 \text{ mM}, E = 0.062 \text{ V}$

Table 1.5 Lifetimes of elemental mercury based on reactions with selected atmospheric oxidants. Adapted (41)

Reaction	Rate Constant	Typical Concentration	KH, 298 (M atm ⁻¹)	Aqueous Concentration (M)	Lifetime (s)
$\text{Hg}^0(\text{aq}) + \text{HOBr}(\text{aq}) \leftrightarrow \text{Hg}^{2+}(\text{aq}) + \text{OH}^-(\text{aq}) + \text{Br}^-$	$0.279 \text{ M}^{-1} \text{ s}^{-1}$	270 pptv	48	1.3×10^{-5}	2.8×10^5
$\text{Hg}^0(\text{aq}) + \text{Br}_2(\text{aq}) \leftrightarrow \text{Hg}^{2+}(\text{aq}) + \text{Br}^-$	$0.196 \text{ M}^{-1} \text{ s}^{-1}$	2.5 pptv	0.68	1.7×10^{-9}	3.0×10^9
$\text{Hg}^0(\text{aq}) + \text{OBr}^-(\text{aq}) + \text{H}^+ \leftrightarrow \text{Hg}^{2+}(\text{aq}) + \text{OH}^-(\text{aq}) + \text{Br}^-$	$0.273 \text{ M}^{-1} \text{ s}^{-1}$	15 pptv	48	7.2×10^{-7}	5.1×10^6

Table 1.6 Aqueous phase chemistry. Adapted (39)

Equilibrium	K [M⁻¹]
$\text{Hg}^{2+} + \text{OH}^- \rightleftharpoons \text{HgOH}^+$	4.00E+10
$\text{HgOH}^+ + \text{OH}^- \rightleftharpoons \text{Hg(OH)}_2$	1.58E+11
$\text{Hg}^{2+} + \text{SO}_3^{2-} \rightleftharpoons \text{Hg(SO}_3)_2^{2-}$	2.00E+13
$\text{HgSO}_3 + \text{SO}_3^{2-} \rightleftharpoons \text{Hg(SO}_3)_2^{2-}$	1.00E+10
$\text{Hg}^{2+} + \text{Cl}^- \rightleftharpoons \text{HgCl}^+$	5.80E+06
$\text{HgCl}^+ + \text{Cl}^- \rightleftharpoons \text{HgCl}_2$	2.50E+06
$\text{HgCl}_2 + \text{Cl}^- \rightleftharpoons \text{HgCl}_3^-$	6.70E+00
$\text{HgCl}_3^- + \text{Cl}^- \rightleftharpoons \text{HgCl}_4^{2-}$	1.30E+01
$\text{Hg}^{2+} + \text{Br}^- \rightleftharpoons \text{HgBr}^+$	1.10E+09
$\text{HgBr}^+ + \text{Br}^- \rightleftharpoons \text{HgBr}_2$	2.50E+08
$\text{HgBr}_2 + \text{Br}^- \rightleftharpoons \text{HgBr}_3^-$	1.50E+02
$\text{HgBr}_3^- + \text{Br}^- \rightleftharpoons \text{HgBr}_4^{2-}$	2.30E+01
$\text{HgOH}^+ + \text{Cl}^- \rightleftharpoons \text{HgOHCl}$	2.69E+07

reactivity in aqueous solutions.

The final remarks of the Xie et al. (39) study were (1) The reaction of mercury with Br dominates the loss of atmospheric elemental mercury detected in arctic regions; (2) BrHgOBr is the most abundant reactive mercury species, both in the gas phase and in the aqueous phase.

Therefore, if mercury is oxidized in the liquid phase by bromine, some parallel reactions between bromine and SO₂ can be occurring, decreasing the amount of bromine available to oxidize the mercury and increasing the amount of elemental mercury in the gas phase. Also, this increase in elemental mercury could be generated by a reduction of oxidized mercury back to elemental as presented in the following section.

Reduction of Oxidized Mercury Back to Elemental

The bias in elemental mercury measurements when both bromine and SO₂ are present in the system could be generated from the reduction of oxidized mercury species back to elemental by interactions of mercury with some species derived from SO₂ in the liquid phase.

Chang et al. (54) investigated the potential for reduction of Hg²⁺ to Hg⁰ under wet FGD scrubber conditions and the process factors that can affect the extent of the Hg⁰ re-emission. A bench-scale wet scrubber simulator (WSS) contained different compositions of the scrubbing liquor. The temperature was controlled between 50-60°C by a water bath. The elemental mercury vapor concentration was measured using a UV analyzer (Buck 400A). The main conclusions of this study were: (1) The Hg²⁺ reduction/Hg⁰ emission increases as the S(IV) decreases. (2) The elemental mercury re-emission will be higher for a forced oxidation FGD scrubber than for a natural oxidation because of the lower S(IV) concentration of the latter.

Dombrowski et al. (59) studied the effect of the calcium bromide injection on mercury oxidation. The tests were performed at Plant Miller Unit 4 which is a 700 MW pulverized coal unit that burns PRB. The unit is equipped with a SCR and a cold-side electrostatic precipitator (ESP). The authors incorporated a pilot wet FGD scrubber at the ESP outlet. They determined that the net mercury removal by the calcium bromide injection was difficult to determine due to mercury re-emissions when the SCR was not in operation, both during baseline (0 to 33% oxidized Hg re-emitted) and bromide injection testing (0 to 21% oxidized Hg re-emitted).

Mercury re-emission was not observed when the SCR was in operation (no NH_3) during either baseline or bromide injection testing. Dombrowski et al. (59) determined that the speciation of HBr and Br_2 in SO_2 -rich boiler flue gas by wet impinger techniques was not possible, due to the immediate reduction of water-soluble Br_2 back to HBr by absorbed SO_2 . For injection rates from 25 to 234 ppm Br added to the coal, the measured flue gas bromide concentrations were 50–60 % of theoretical predictions, assuming that all injected calcium bromide converted to flue gas HBr or Br_2 . The “missing” bromine was not found in the fly ash and may be a result of measurement biases associated with Method 26. The removal of total bromine across the FGD scrubber ranged from 94 – 96%, which was similar to the SO_2 scrubbing efficiency of the FGD system. The FGD scrubber efficiently removed bromine from the flue gas.

The focus of the study developed by DeBerry et al. (55) was to obtain kinetic data about the reduction of oxidized mercury back to elemental at conditions typical of a wet FGD system. They evaluated the effect of different SO_2 -derived species as well as chloride and thiosulfate, species which form strong complexes with oxidized mercury. The effect of the pH in the reduction of oxidized mercury back to elemental was also studied because it affects the partitioning of the sulfite species and the kinetics of some reactions. The effects of temperature and ionic strength were also measured. DeBerry et al. (55) performed their study at temperatures in the range of normal operation of an FGD 50-55°C. Based on their results, the authors concluded that mercury re-emissions in a full-scale wet FGD could be greatly affected for the pH change in the slurry, sulfite pick up and sulfite oxidation within the absorber rather than reaction tank conditions. As an example, a change in the chloride concentration from zero to 10 mM represented a

decrease in the mercury re-emission of about 90 %. DeBerry et al. (55) also proposed a kinetic mechanism to describe liquid phase interactions among mercury, chloride, sulfites and thiosulfate. The model, shown in Figure 1.4, predicts the experimental results for the effect of pH, sulfite and chloride:

In an extension of this work, Blythe et al. (59) found that changing 100mM chloride by 100 mM bromine in the FGD liquor at pH= 5 with 5 mM sulfite, reduced the elemental mercury re-emissions from 2.2 to 0.7 $\mu\text{g}/\text{Nm}^3$ approximately.

Ghorishi et al. (56) studied the fundamentals and methods of mitigation of elemental mercury emissions from wet scrubbers. Their reaction model described the gas and liquid phase interactions of sulfides as well as redox and ion-ion equilibrium reactions. In their reaction scheme, S(IV) accelerates the elemental mercury re-emissions by consuming oxygen at the gas-liquid interface. The overall reaction also demonstrated that lowering the pH results in lower mercury re-emissions. Field tests of the additive developed by B&W were performed at two coal-fired utilities with different size and wet FGD chemistry. Some of the concluding remarks of the work by Ghorishi et al. (56) were: (1) In the absence of sulfides in the wet scrubber the two most influential parameters in elemental mercury re-emissions were the concentration of oxygen in the flue gas and the concentration of S(IV) in the scrubber liquor. (2) The pH of the scrubber becomes important when the consumption of sulfides by metal ions generated mostly from the limestone is accounted for. (3) Field tests suggested that the use of sodium hydrosulfide is a good approach to decrease elemental mercury re-emissions because the precipitation of HgS becomes more significant than the reduction of oxidized mercury back to elemental.

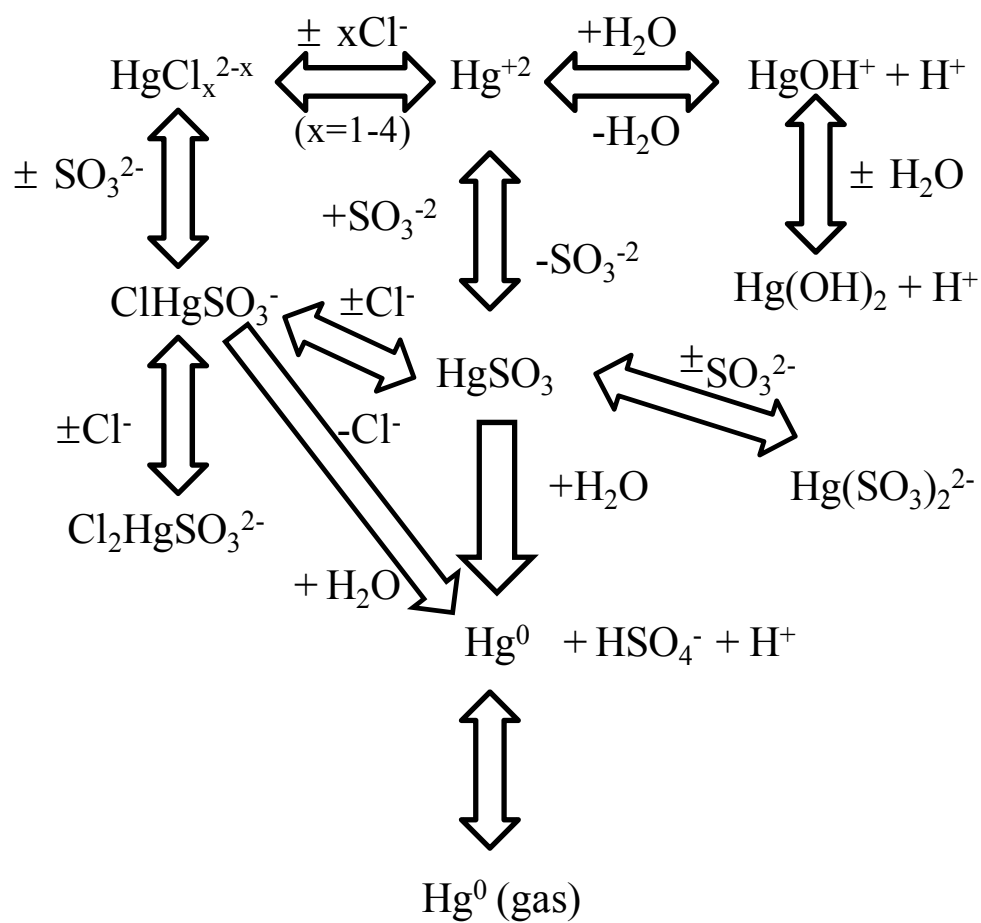


Figure 1.4. Liquid phase interactions among mercury, chloride, sulfites and thiosulfate. Adapted (54)

From all these studies, it is observed that the pH of the solution related to the concentration of SO_2 and the presence and type of FGD in the combustion system are crucial factors for the presence of reduction reactions involving oxidized mercury and SO_2 species.

Gas-phase Reaction Pathways for Mercury Oxidation by Chlorine

A number of researchers have proposed models of the kinetics of gas-phase oxidation of mercury by chlorine. Among the kinetic schemes considered were those of Niksa et al. (60) who studied the kinetics of homogeneous mercury oxidation by chlorine using two approaches. First, they accounted for the major Cl-mercury interactions and the effect of other flue gas component such as NO. Second, they validated their mechanism against the available experimental data for which the HCl was the major oxidant species. The submechanism developed by Niksa et al. (60) is presented in Table 1.7. Based on the comparison of the model predictions with the available experimental data of mercury oxidation by chlorine, they determined that the overall reaction pathway is constituted by the oxidation of elemental mercury by Cl to produce HgCl which is further oxidized by Cl_2 to generate HgCl_2 with a parallel regeneration of Cl-atoms.

Wilcox et al. (61) determined some of the rate constants for mercury oxidation by chlorine using ab initio methods of quantum chemistry. The mechanism extracted from their study contains the set of reactions shown in Table 1.8. Wilcox's rate constants are generally two or three orders of magnitude lower than those predicted by Niksa et al. (60), particularly for reactions where the main oxidation product, HgCl_2 , was formed.

Xu et al. (62) studied the kinetics of the homogeneous mercury reactions in flue gas or simulated flue gas. Based on previous publications about the effect of chlorine on

**Table 1.7. Hg⁰ Oxidation submechanism UConn Hg-Cl kinetic mechanism.
Adapted (35, 60, 63, 64)**

Reaction	A (mol-cm-s-K)	n	E _a (cal/mol)
Hg+Cl+M=HgCl+M	9.00E+15	0.5	0
Hg+Cl ₂ =HgCl+Cl	3.26E+10	0	22800
Hg+HOCl=HgCl+OH	3.43E+12	0	12790
Hg+HCl=HgCl+H	4.94E+14	0	79300
HgCl+Cl ₂ =HgCl ₂ +Cl	2.02E+14	0	3280
HgCl+HCl=HgCl ₂ +H	4.94E+14	0	21500
HgCl+Cl+M=HgCl ₂ +M	1.16E+16	0.5	0
HgCl+HOCl=HgCl ₂ +OH	4.27E+13	0	1000

Rate constant $k = AT^n \exp(-E_a/RT)$; A, n and E_a are the preexponential factor; unit less power and the activation energy respectively.

**Table 1.8. Hg⁰ Oxidation submechanism Wilcox Hg-Cl kinetic mechanism.
Adapted (61)**

Reaction	A (mol-cm-s-K)	n	E _a (cal/mol)
HgCl+M=Hg+Cl+M	4.25E+13	0	16100
Hg+Cl ₂ =HgCl+Cl	1.34E+12	0	42800
Hg+HOCl=HgCl+OH	3.09E+13	0	36600
Hg+HCl=HgCl+H	2.62E+12	0	82100
HgCl+Cl ₂ =HgCl ₂ +Cl	2.47E+10	0	0
HgCl+HCl=HgCl ₂ +H	3.11E+11	0	30270
HgCl ₂ +M=HgCl+Cl+M	2.87E+13	0	80600
HgCl+HOCl=HgCl ₂ +OH	3.48E+10	0	0
HgCl ₂ +M=Hg+Cl ₂ +M	3.19E+11	0	87000

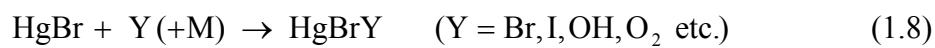
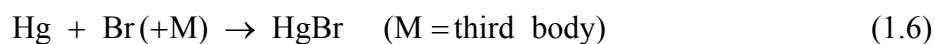
mercury oxidation and the proposed reaction mechanisms for mercury-chlorine interactions, Xu et al. (62) extended the available set of reactions to include additional species such as HgO and calculated new reaction constants using transition state theory. The model predictions were compared to available experimental data of mercury chlorine reactions. Xu et al. (62) found that their model predictions were only able to describe one out of three sets of the literature data used to validate their model. They suggested that the addition of the HgO reactions in their model, the lack of accurate rate constants for the proposed mechanisms and some heterogeneous interactions could be the causes for the poor agreement between model predictions and experimental data. Their sensitivity analysis showed that the reactions involving HgO are in fact more important in terms of the extent of mercury oxidation than the basic reactions suggested by previous studies (Hg- Cl reactions). The Xu et al. (62) mechanism is shown in Table 1.9.

Table 1.9. Hg⁰ Oxidation submechanism Xu 2003 Hg-Cl kinetic mechanism. Adapted (62)

Reaction	A (mol-cm-s-K)	n	E _a (cal/mol)
Hg + Cl + M = HgCl + M	2.40E+08	1.4	-1.44E+04
Hg + Cl ₂ = HgCl + Cl	1.39E+14	0	3.40E+04
Hg + HOCl = HgCl + OH	4.27E+13	0	1.90E+04
Hg + HCl = HgCl + H	4.94E+14	0	7.93E+04
HgCl + Cl ₂ = HgCl ₂ + Cl	1.39E+14	0	1.00E+03
HgCl + HCl = HgCl ₂ + H	4.94E+14	0	2.15E+04
HgCl + Cl + M = HgCl ₂ + M	2.19E+18	0	3.10E+03
HgCl + HOCl = HgCl ₂ + OH	4.27E+13	0	1.00E+03
Hg + ClO = HgO + Cl	1.38E+12	0	8320
HgO + HCl = HgCl + OH	9.63E+04	0	8920
HgO + HOCl = HgCl + HO ₂	4.11E+13	0	60470
Hg + ClO ₂ = HgO + CO	1.87E+07	0	51270

Gas-Phase Reaction Pathways for Mercury Oxidation by Bromine

Compared to chlorine, experimental and modeling data for mercury oxidation by bromine are scarce. Many of the available models correspond to atmospheric conditions (50, 53). For this study, a number of the published kinetic data were evaluated, among them the work by Goodsite et al. (50) which used the Rice-Ramsberger-Kassel-Marcus (RRKM) theory to study the rate coefficient for the reaction between mercury and Br under temperature conditions typical of a marine boundary layer. The mechanism used by the authors in this study included the following reactions:



The authors concluded that the recombination of mercury with bromine is fast due to the high density of vibrational states arising from the low vibrational frequency and small rotational constant of HgBr. Then the transformation of elemental to oxidized mercury occurs by recombination of elemental mercury with Br. After that, there is a competition between further addition of Br to form HgBr₂ or thermal decomposition of HgBr.

Niksa et al. (65, 66) proposed a mechanism for interactions Br/Hg/Cl based on the available literature and compared their model predictions with experimental data obtained from field tests at plants Miller, Milton R. Young, and Monticello. The mechanism included the reactions shown in Table 1.10.

The authors concluded that the model accurately predicts the impact of bromine

Table 1.10 Reactions of Hg/Br in the gas phase mechanism. Adapted (65, 66)

Reactions	A	n	Ea (kcal/mol)
$\text{Hg}^0 + \text{Br} + \text{M} \leftrightarrow \text{HgBr} + \text{M}$	$6.94 \times 10^{14} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$	0.5	0
$\text{Hg}^0 + \text{Br}_2 \leftrightarrow \text{HgBr} + \text{Br}$	$1.15 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	0	31.8
$\text{Hg}^0 + \text{HBr} \leftrightarrow \text{HgBr} + \text{H}$	$3.78 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	0	75.7
$\text{Hg}^0 + \text{BrOH} \leftrightarrow \text{HgBr} + \text{OH}$	$3.52 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	0	36.9
$\text{HgBr} + \text{Br}_2 \leftrightarrow \text{HgBr}_2 + \text{Br}$	$1.11 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	0	0.5
$\text{HgBr} + \text{Br} + \text{M} \leftrightarrow \text{HgBr}_2 + \text{M}$	$8.83 \times 10^{14} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$	0.5	0
$\text{HgBr} + \text{HBr} \leftrightarrow \text{HgBr}_2 + \text{H}$	$1.16 \times 10^7 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	2.5	28.1
$\text{HgBr} + \text{BrOH} \leftrightarrow \text{HgBr}_2 + \text{OH}$	$3.47 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	0	5.5
$\text{Hg} + \text{BrCl} \leftrightarrow \text{HgBr} + \text{Cl}$	$1.39 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	0	32.1
$\text{HgBr} + \text{Cl}_2 \leftrightarrow \text{HgBrCl} + \text{Cl}$	$1.39 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	0	1
$\text{HgBr} + \text{Cl} + \text{M} \leftrightarrow \text{HgBrCl} + \text{M}$	$1.16 \times 10^{15} \text{ cm}^3 \text{ mol}^{-2} \text{ s}^{-1}$	0.5	0
$\text{HgBr} + \text{HCl} \leftrightarrow \text{HgBrCl} + \text{H}$	$4.64 \times 10^3 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	2.5	18.2
$\text{HgBr} + \text{HOCl} \leftrightarrow \text{HgBrCl} + \text{OH}$	$4.27 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	0	3.3

addition on mercury oxidation. They suggested bromine as an effective mercury control strategy for plants that burn low-rank coals because it dramatically accelerates the rates of mercury oxidation for both in-flight and across the SCRs.

Bozzeli et al. (67) are still working on their own detailed kinetic mechanism to explain some of the main bromine-mercury interactions. So far their proposed mechanism includes the reactions presented in Table 1.11.

Donohoue et al. (68) used a pulsed laser photolysis-pulsed laser induced fluorescence technique to study the recombination of mercury and bromine atoms and the self-reaction of bromine atoms represented by the reactions:



Table 1.11 Bozzelli 2010 Hg-Br kinetic mechanism. Adapted (67)

Reaction	A (mol-cm-s-K)	n	Ea (cal/mol)
$\text{HG} + \text{BR} \rightleftharpoons \text{HGBR}$	5.20E+18	-2.86	461
$\text{HG} + \text{BR}_2 = \text{HGBR} + \text{BR}$	9.94E+20	-2.42	28933
$\text{HGBR} + \text{H} \rightleftharpoons \text{HG} + \text{HBR}$	2.70E+13	0	2300
$\text{HGBR} + \text{OH} \rightleftharpoons \text{HG} + \text{HOBR}$	3.27E+12	0	1000
$\text{HGBR} + \text{BR}_2 \rightleftharpoons \text{HGBR}_2 + \text{BR}$	7.39E+12	0	1000
$\text{HGBR} + \text{BR} \rightleftharpoons \text{HGBR}_2$	3.80E+24	-4.17	1974
$\text{HGBR}_2 + \text{H} \rightleftharpoons \text{HGBR} + \text{HBR}$	4.64E+03	2.5	1910
$\text{HGBR} + \text{HOBR} \rightleftharpoons \text{HGBR}_2 + \text{OH}$	2.27E+12	0	1700
$\text{HGBR} + \text{CL}_2 = \text{HGBRCL} + \text{CL}$	6.70E+12	0	1250
$\text{HGBR} + \text{BRO} = \text{HGBR}_2 + \text{O}$	2.25E+12	0	1150
$\text{HGBR} + \text{O} = \text{BRO} + \text{HG}$	3.35E+13	0	1300
$\text{HGCL} + \text{BR}_2 = \text{HGBRCL} + \text{BR}$	8.20E+11	0	1050
$\text{HGOH} + \text{BR} \rightleftharpoons \text{HGBROH}$	1.57E+30	-7.28	1903
$\text{HGOH} + \text{BR} \rightleftharpoons \text{HGBR} + \text{OH}$	6.67E+13	-0.36	218
$\text{HGBR} + \text{OH} \rightleftharpoons \text{HGBROH}$	2.19E+29	-5.77	2976
$\text{HGO} + \text{BR} \rightleftharpoons \text{HGBRO}$	8.29E+24	-4.75	1735
$\text{HGBROH} + \text{OH} = \text{HGBRO} + \text{H}_2\text{O}$	2.45E+12	0	850
$\text{HGBRO} + \text{HO}_2 = \text{HGBROH} + \text{O}_2$	5.50E+11	0	0
$\text{HG} + \text{BR}_2 = \text{HGBR}_2$	1.19E+11	-0.01	4736

The pressure range considered for the study was 200-600 Torr and the temperature range was 243-293K. At these conditions, the authors observed that for both reactions, the pressure and temperature dependencies are consistent with a three-body recombination. Also they determined that the recombination of mercury and bromine atoms is dependent on the stability and reactivity of the HgBr species.

The analysis of the production rates of HgBr₂ performed by Niksa et al. (35) shows that elemental mercury is primarily consumed to form HgBr through the reaction $\text{Hg}^0 + \text{Br} + \text{M} = \text{HgBr} + \text{M}$. The HgBr can either decompose at high temperatures or be further oxidized to HgBr₂ by Br₂ at moderate temperatures through the reaction $\text{HgBr} +$

$\text{Br}_2 = \text{HgBr}_2 + \text{Br}$, which regenerates Br species consumed in the first reaction (34, 69). This two-step mechanism is in agreement with the one proposed by Donohue et al. (68) to explain mercury-bromine interactions under atmospheric conditions. The overall oxidation mechanism for mercury-bromine, can be represented by Figure 1.5:

Oxy-Fuel Mercury Oxidation

Interactions between mercury and other flue gas components can be affected by a change in combustion conditions. In recent years, global climate change and its dependence on green house gas emissions has become an important topic of study. The main objective is to decrease the emissions of CO_2 . Coal combustion is one of the major sources of CO_2 , and these studies are focused on estimating the cost and performance of different coal combustion technologies that aid CO_2 capture and sequestration. Among these emerging technologies is the combustion of pulverized coal under oxy-fuel conditions. Oxy-firing offers the possibility of CO_2 capture by direct compression of the flue gas which consists basically of CO_2 (17). These combustion conditions offer a new environment for mercury oxidation where the influence of some flue gas components such as chlorine, bromine and SO_2 could change. Suriyawong et al. (18) used different oxygen-nitrogen or oxygen-carbon dioxide mixtures in a fluidized bed reactor connected to an alumina tubular reactor at 1200°C . They found that the extent of mercury oxidation was not dependent on the composition of the gas mixture. However, in a later study Suriyawong et al. (19) found a higher concentration of oxidized mercury when the carrier gas was a mixture $\text{O}_2\text{-CO}_2$ and chlorine. To date, there are no additional reports that the author is aware of on the effect of flue gas components on mercury oxidation under oxy-fuel combustion.

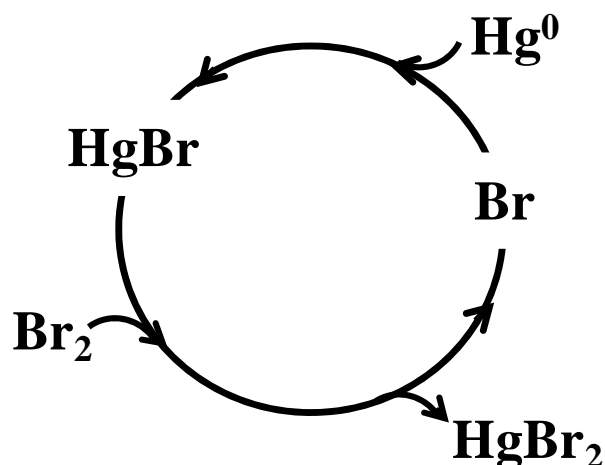


Figure 1.5. Conversion cycle for homogeneous Hg^0 oxidation by Br species. Adapted(68)

Heterogeneous Mercury Oxidation

As mentioned early in the literature review, some heterogeneous interactions can affect the extent of mercury oxidation reported by some studies. These interactions are generated mostly from the presence of ash and carbon in the system. To understand the type of interactions that could be occurring in some combustion systems, a review of previous publications is presented below.

Species such as SO_2 , chlorine, bromine, and NO_x have an effect on the efficiency of activated carbons for mercury adsorption and oxidation. Presto et al. (70) studied the effect of SO_2 on mercury adsorption using Norit Darco FGD and Norit Darco Hg-LH activated carbons at a bed temperature of 149°C . They found that SO_2 inhibits adsorption and that this could be explained by the competitive adsorption of SO_2 . Bhardwaj et al. (71) observed an increase in mercury uptake capacity for the Norit Darco FGD sorbent exposed to a flue gas consisting of 6% O_2 , 13.5% CO_2 , 6 % H_2O , 20 ppm NO_2 , 300 ppm NO , N_2 balance at 140°C in absence of acid gases such as SO_2 .

Other studies suggest that the SO_2 could improve elemental mercury adsorption on carbon. Ghorishi et al. (15) studied the effect of acid gases on mercury species sorption on activated carbons. At a temperature of 100-140°C, using a Norit Darco powdered activated carbon and a flue gas composed of nitrogen, HgCl_2 and 1000 ppm SO_2 , they concluded that SO_2 reacted with the activated carbon and created sulfur active sites, which are active in capturing elemental mercury through formation of solid-phase S-Hg bonds.

Miller et al. (72) observed an initial mercury capture of 50%, which decreased to only 10% capture after 1 hour with no oxidation of elemental mercury in presence of 1600 ppm SO_2 . In this case the flue gas composition was 6 % O_2 , 12 % CO_2 , 8% H_2O , balance N_2 ; the activated carbon was LAC and the temperature was 107°C. They concluded that SO_2 alone has a small benefit on elemental mercury capture.

Previous studies suggest that the effect of hydrochloric acid on mercury oxidation and adsorption is that of increasing mercury adsorption. Using a flue gas composition that was 6 % O_2 , 12 % CO_2 , 8% H_2O , balance N_2 and the LAC activated carbon with the bed temperature set at 107°C, Miller et al. (72) observed a nearly 100% mercury capture in the presence of 50 ppm HCl, which indicates that the HCl alone has a significant benefit. The enhancement effect of HCl on elemental mercury capture by a lignite powdered activated carbon was also observed by Carey et al. (16), who conclude that despite the lower gas-phase concentration, HCl had a more pronounced enhancement effect on elemental mercury capture than other species present in the flue gas such as SO_2 , suggesting that the Cl sites are more active than the S sites. Using lignite powdered activated carbon exposed to a flue gas composed of nitrogen, elemental mercury and 50

ppm HCl Ghorishi et al. (15) found that HCl can react with the lignite sorbent and creates chlorine (Cl) sites; these sites are instrumental in capturing elemental mercury through formation of Cl-Hg bonds in the solid phase.

The effect of nitrogen monoxide (NO) on the carbon efficiency for mercury oxidation was studied by Lui et al. (73) He used a fixed-bed reactor charged with 100 mg of 60-80 mesh size, virgin, Calgon granulated activated carbon or sulfur-impregnated activated carbon (SIAC). His carbon bed was operated at 140°C using a carrier gas flow rate of 1 L/min. The authors concluded that the weight of both the granulated activated carbon and SIAC samples remained unchanged upon exposure to 100 ml/min of 400 ppm NO in N₂ after 5 hours of exposure at 140°C. It was postulated that NO was not adsorbed by the carbon at the conditions tested. One explanation for that could be the extremely low NO concentration used and the low temperature used. The efficiency of the carbons for mercury adsorption was not affected by the presence of NO.

The investigation of the oxidation rate of elemental mercury by Br₂ under flue gas conditions downstream from the air preheater and upstream from the particulate collectors was performed by Liu et al. (73). They monitored the concentration of elemental mercury as a function of time in Pyrex flasks by a mercury cold vapor atomic absorption spectrophotometer (CVAAS). The elemental mercury concentrations employed were 0.01 ppm-0.20 ppm, with Br₂ ranging between 4 and 60 ppm and fly ash was used as sorbent. It was observed that the SO₂ slightly inhibited the elemental mercury removal by fly ash at the typical flue gas temperatures. In contrast, a little increase in the elemental mercury removal by Br₂ was observed when NO was present in the flue gas. At 298 K fly ash in the flue gas significantly promoted the oxidation of

elemental mercury by Br_2 , and the unburned carbon component played a major role in the promotion primarily through the rapid adsorption of Br_2 which effectively removed elemental mercury from the gas phase.

Benson et al. (47) studied cost-effective alternatives for oxidizing the elemental mercury in lignite-based combustion flue gases into a more soluble and reactive mercury compound (Hg^{2+}) that could increase the efficiency of some of the existing pollutant control devices for mercury removal. They performed their tests using the Milton R. Young (MRY) station at Minnkota Power Cooperative. MRY Station Unit 2 is a 450-MW cyclone unit near Center, North Dakota. A cold-side electrostatic precipitator (ESP) and a flue gas desulfurization (FGD) unit are used at MRY for controlling particulate and sulfur dioxide (SO_2) emissions. The authors found that an injection rate of CaBr_2 corresponding to a 113 ppm bromine concentration in the coal, was enough to keep the scrubber outlet mercury concentration below $5 \mu\text{g/dNm}^3$.

Benson et al. (47) also studied the effects of the calcium bromide injections on mercury oxidation. The full-scale tests were performed at Southern Company's Plant Miller Unit 4 firing PRB coal. Unit 4 has an electrostatic precipitator (ESP) for particulate control and a selective catalyst reduction (SCR) unit for NO_x control. The authors found that increasing the average bromine injection rate from 3 to 86 ppm in the coal caused the mercury oxidation to increase from 86 to 92 %. The results showed that the injection of calcium bromide into the furnace holds promise for converting elemental mercury to oxidized mercury and improving mercury removal for Powder River Basin (PRB) fired units.

These experimental observations are of great value for determining the effects that heterogeneous interactions have on mercury speciation and oxidation. However, a more detailed understanding of the surface chemistry and kinetics of the heterogeneous reactions occurring in combustion systems is even more important for the design of effective technologies for mercury emissions mitigation.

Olson et al. (74-76) studied the chemisorption mechanisms of mercury on activated carbons. Based on a factorial design of experiments, the authors evaluated different powdered carbons using a thin fixed bed system exposed to a simulated flue gas composition with variable composition of acid gases such SO_2 , NO_2 , and HCl combined with a base mixture of N_2 , O_2 , NO , CO_2 and H_2O (l). The temperature of the bench-scale system was controlled between 100-150⁰C. When the only acid gas present in the flue gas is NO_2 , very little breakthrough was observed by the authors for long periods of time, indicating a very stable form of mercury bound (76). This strong bond is attributed to the oxidation of elemental mercury with the reduction of NO_2 to form oxidized species that have very low volatility. When SO_2 was added to the flue gas containing SO_2 , the authors observed that the higher the SO_2 concentration the shorter the breakthrough time. These breakthrough times are consistent with the theory that the SO_2 poisons the active sites for the adsorption of oxidized mercury. Based on their experimental observations of breakthrough times and the effect of different acid gases on the extent of mercury oxidation and adsorption, the authors postulated that the carbon sorbents have two or more independent reaction sites with at least an oxidation site and a binding site for the oxidized mercury (76). The oxidation site is defined as an electron-accepting Lewis acid site and the oxidized mercury bonding site is an electron-donating basic site. As

mentioned above, acid species such SO_2 can poison the active sites for the adsorption of oxidized mercury species. However, this poisoning effect does not affect the oxidation sites. Olson et al. (74-76) have performed extensive work on the Lewis acid basic binding site with the purpose of detailing the nature of the carbon site and its interaction with flue gases and mercury.

References

1. <http://www.epa.gov/hg/regs.htm>.
2. <http://www.eia.doe.gov>.
3. Controlling power plant emissions: controlling mercury with existing controls. http://www.epa.gov/mercury/control_emissions/tech_exist.htm.
4. http://www.mercury.utah.gov/atmospheric_transport.htm.
5. Procaccini, C., Bozzelli, J., Longwell, J., Smith, K., Sarofim, A. Presence of Chlorine Radicals and Formation of Molecular Chlorine in the Post-Flame Region of Chlorocarbon Combustion. *Environ. Sci. Technol.* **2000**, 34 (21), 4565-4570.
6. Cao, Y., Duan, Y., Kelli, S., Li, L., Xu, W., Riley, J., Pan, W. Impact of Coal Chlorine on Mercury Speciation and Emission from a 100-MW Utility Boiler with Cold-Side Electrostatic Precipitators and Low-NO_x Burners. *Energy Fuels* **2005**, 19, 842-854.
7. Sliger R., Kramlich, J., Marinov, N. Towards the Development of a Chemical Kinetic Model for the Homogeneous Oxidation of Mercury by Chlorine Species. *Fuel Process. Technol.* **2000**, 65–66, 423–438.
8. Laudal D., Brown, T., Nott, B. Effect of Flue Gas Constituents on Mercury Speciation. *Fuel Process. Technol.* **2000**, 65–66, 157–165.
9. Agarwal, H., Stenger, H., Effects of H₂O, SO₂, and NO on Homogeneous Hg Oxidation by Cl₂. *Energy Fuels* **2006**, 20, 1068-1075.
10. Ehrhardt, K., Rohde, A., Bockorn, H., Bozzelli, J. “Prediction of the Cl₂ and Br₂ Content in Flue Gases and Selection Reduction of Cl₂ and Br₂ by H₂ Injection for Fuel-lean conditions.” Proceedings of the 6th European Conference on Industrial Furnaces and Boilers, Estoril-Lisboa, Portugal, April 2-5, 2002.
11. Vosteen, B., Kanefke, R., Köser, H. Bromine-enhanced Mercury Abatement from Combustion Flue Gases- Recent Industrial Applications and Laboratory Research. *VGB Power Tech.* **2006**, 86, 70-75.
12. Li, Z., Sun, X., Luo, J., Hwang, J. Unburned Carbon from Fly Ash for Mercury Adsorption: II. Adsorption Isotherms and Mechanisms. *J Miner. Mater. Charact. Eng.* **2002**, 1 (2), 79-96.
13. Wang, L., Chen, C., Kolker, K. Vapor-phase Elemental Mercury Adsorption by Residual Carbon Separated from Fly Ash. *J. Environ. Sci.* **2005**, 17(3), 518-520.

14. Lopez-Anton, M., Abad-Valle, P., Diaz-Somoano, M., Suarez-Ruiz, I., Martinez-Tarasona, R. The Influence of Carbon Particle Type in Fly Ashes on Mercury Adsorption. *Fuel* **2009**, 88, 1194-1200.
15. Ghorishi, B., Gullet, B. Sorption of Mercury Species by Activated Carbons and Calcium-based Sorbents: Effect of Temperature, Mercury concentration and Acid Gases. *Waste Manage. Res.* **1998** 16 6 582 - 593.
16. Carey, T., Hargrove, O., Richardson, C., Change, R., Meserole, F. *Performance of Activated Carbon for Mercury Control in Utility Flue Gas Using Sorbent Injection*. in: Proceedings of the First EPRI-DOE-EPA Combined Utility Air Pollutant Control Symposium (the "Mega "Symposium), Washington, DC, USA, August 25-29, 1997.
17. <http://web.mit.edu/coal/>.
18. Suriyawong, A., Gamble, M., Lee, M., Axelbaum, R., Biswas, P. Submicrometer Particle Formation and Mercury Speciation Under O₂-CO₂ Coal Combustion. *Energy Fuels* **2006**, 20, 2357-2363.
19. Suriyawong, A. Skeen, P. Biswas and R. Axelbaum. *Lab-Scale Studies of Oxy-fuel Combustion*. www.netl.doe.gov/publications/proceedings/08/ucr/abstracts/Axelbaum_Abstract.pdf - 2010-05-25.
20. Senior C. *Behavior of Mercury in Air Pollution Control Devices on Coal-Fired Utility Boilers*. Presented for Power Production in the 21st Century: Impact of Fuel Quality and Operations. Engineering Foundation Conference, Snowbird, UT, October 28–November 2, 2001
21. Senior, C., Helble, J., Sarofim, A. Emissions of Mercury, Trace Elements, and Fine Particles from Stationary Combustion Sources. *Fuel Process. Technol.*, **2000**, 65-66, 263-288.
22. DeVito, M., Rosenhoover, W. *Flue Gas Mercury and Speciation Studies at Coal-Fired Utilities Equipped with Wet Scrubbers*, in: 15th International Pittsburgh Coal Conference, Pittsburgh, PA, September 15–17, 1998.
23. Laudal, D. *Mercury Speciation Sampling at Cooperative and United Power Associations Coal Creek Station*, Final Report, Energy and Environmental Research Center, University of North Dakota, January 1999.
24. Galbreath, C., Zygarlicke, C. Mercury Transformations in Coal Combustion Flue Gases. *Fuel Process. Technol.*, **2000**, 65-66, 289-310.

25. Hall, B., Schager, P., Weesmaa, J. The Homogeneous Gas Phase Reaction of Mercury with Oxygen, and the Corresponding Heterogeneous Reactions in the Presence of Activated Carbon and Fly Ash. *Chemosphere*. **1995**, 30, 611–627.
26. Hall, B., Lindqvist, O., Ljungstro, E. Mercury Chemistry in Simulated Flue Gases Related to Waste Incineration Conditions, *Environ. Sci. Technol.* **1990**, 24, 108–111.
27. Laudal, D., Brown, T., Nott, B., Chu, P. *Bench-scale Studies to Determine the Effects of Flue Gas Constituents on Mercury Speciation*, Conference on Air Quality: Mercury, Trace Elements, and Particulate Matter, McLean, VA, December 1–4, 1998.
28. Singer J. D. *Combustion Fossil Power Systems, Combustion Engineering*; 3rd ed.; Windsor, CT, 1981.
29. Zhao, L., Rochelle, G. Mercury Absorption in Aqueous Oxidants Catalyzed by Mercury_II, *Ind. Eng. Chem. Res.* **1998**, 37, 380–387.
30. Aylett, B. *The Chemistry of Zinc, Cadmium, and Mercury*, Pergamon Texts in Inorganic Chemistry, Vol. 18, 1975.
31. Schroeder, W., Yarwood, G., Niki, H. Transformation Processes Involving Mercury Species in the Atmosphere, Results from a Literature Survey. *Water Air Soil Pollut.* **1991**, 56, 653–666.
32. Goodsite, M., Plane, J., Skov, H. A Theoretical Study of the Oxidation of Hg^0 to HgBr_2 in the Troposphere. *Environ. Sci. Technol.* **2004**, 38, 1772–1776.
33. Ariya, P., Khalizov, A., Gidas, A. Reactions of Gaseous Mercury with Atomic and Molecular Halogens: Kinetics, Product Studies, and Atmospheric Implications. *J. Phys. Chem. A*, **2002**, 106, 7310–7320.
34. Senior, C., Sarofim, A., Zeng, T., Helble, J., Mamani-Paco, R. Gas-phase Transformations of Mercury in Coal-fired Power Plants, *Fuel Process. Technol.* **2000**, 63, 197–214.
35. Niksa, S., Helble, J., Fujiwara, N. Kinetic Modeling of Homogeneous Mercury Oxidation: The Importance of NO and H_2O in Predicting Oxidation in Coal-Derived Systems. *Environ. Sci. Technol.* **2001**, 35, 3701–3706.
36. Cauch, B., Silcox, G., Lighty, J., Wendt, J., Fry, A., Senior, C. Confounding Effects of Aqueous-Phase Impinger Chemistry on Apparent Oxidation of Mercury in Flue Gases. *Environ. Sci. Technol.* **2008**, 42, 2594–2599.

37. Sterling, R., Qiu, J., Helble, J. Experimental Study of Mercury Homogeneous Reaction Chemistry Under Post-Flame Conditions. *Prepr. Pap. Am. Chem. Soc., Div. Fuel Chem.* **2004**, 49 (1), 277-278.
38. *Control of Mercury Emissions from Coal-Fired Electric Utility Boilers*; Interim Report Including Errata Dated 3-21-02," EPA-600/R-01-109, April 2002.
39. Xie, Z., Sander, R., Poschl, U., Slemr, F. Simulation of Atmospheric Mercury Depletion Events (AMDEs) During Polar Springtime Using the MECCA Box Model. *Atmos. Chem. Phys.* **2008**, 7165-7180.
40. Hedgecock, I., Trunfio, G., Pirrone, N., Sprovieri, F. Mercury Chemistry in the MBL: Mediterranean Case and Sensitivity Studies Using the AMCOTS (Atmospheric Mercury Chemistry over the Sea) model. *Atmos. Environ.* **2005**, 39, 7217-7230.
41. Wang, Z., Pehkonen, S. Oxidation of Elemental Mercury by Aqueous Bromine: Atmospheric Implications. *Atmos. Environ.*, **2004**, 38, 3675-3688.
42. Laurier, F., Mason, R., Whalin, L., Kato, S. Reactive Gaseous Mercury Formation in the North Pacific Ocean's Marine Boundary Layer: A Potential Role of Halogen Chemistry. *J. Geophys. Res.* **2003**, 108, 4529- 4541.
43. Platt, U., Honninger, G. The Role of Halogen Species in the Troposphere. *Chemosphere*, **2003**, 52(2), 325-338.
44. Glasow, R., Kuhlmann, R., Lawrence, M., Platt, U., Crutzen, P. Impact of Reactive Bromine Chemistry in the Troposphere. *Atmos. Chem. Phys.* **2004**, 4, 2481- 2497.
45. Yang, X., Cox, R., Warwick, N., Pyle, J., Carver, G., O'Connor, F., Savage, N. Tropospheric Bromine Chemistry and its Impacts on Ozone: A Model Study. *J. Geophys. Res.* **2005**, 110, D23311, 18 PP., doi:10.1029/2005JD006244.
46. Babi, D., Schaedlich F., Schneeberger D. Correction Techniques for Iodine and Bromine Interferences in Continuous Flow Aqueous Mercury Analysis. *Anal. Bioanal. Chem.* **2002**, 374(6), 1022-1027.
47. Benson, S., Holmes, M., McCollor, D., Mackenzie, J., Crocker, C., Kong, L., Galbreath, K., Dombrowski, K., Richardson, C. *Large-Scale Mercury Control Testing for Lignite-Fired Utilities—Oxidation Systems for Wet FGD*; Final Report, DOE NETL DE-FC26-03NT41991, Energy & Environmental Research Center: Grand Forks, ND, March, 2007.
48. Cao, Y., Wang, Q., Chen, C., Chen, B., Cohron, M., Tseng, Y., Chiu, C., Chu, P., Pan, W. Investigation of Mercury Transformation by HBr Addition in a

- Slipstream Facility with Real Flue Gas Atmospheres of Bituminous Coal and Powder River Basin Coal. *Energy Fuels*, **2007**, 21, 2719- 2730.
49. Cao, Y., Gao, Z., Zhu, J., Wang, Q., Huang, Y., Chiu, C., Parker, B., Chu, P., Pan, W. Impacts of Halogen Additions on Mercury Oxidation, in a Slipstream Selective Catalyst Reduction (SCR), Reactor when Burning Sub-Bituminous Coal. *Environ. Sci. Technol.* **2008**, 42, 256-261.
 50. Goodsite, M., Plane, J., Skov, H. A Theoretical Study of the Oxidation of Hg^0 to HgBr_2 in the Troposphere. *Environ. Sci. Technol.* **2004**, 38, 1772-1776.
 51. Qu, Z., Yan, N., Liu, P., Chi, Y., Jia, J. Bromine Chloride as an Oxidant to Improve Elemental Mercury Removal from Coal-Fired Flue Gas. *Environ. Sci. Technol.* **2009**, 43, 8610-8615.
 52. Liu, S., Yan, N., Liu, Z., Qu, Z., Wang, H., Chang, S., Miller, C. Using Bromine Gas to Enhance Mercury Removal from Flue Gas of Coal-Fired Power Plants. *Environ. Sci. Technol.* **2007**, 41, 1405-1412.
 53. Berry, M., Dombrowski, K., Richardson, C., Chang, R., Borders, E., Vosteen, B. *Mercury Control Evaluation of Calcium Bromide Injection into a PRB-Fired Furnace with an SCR*. Presented at Air Quality VI, Arlington, VA, September 24, 27, 2007.
 54. Chang, J., Ghorishi, S. Simulation and Evaluation of Elemental Mercury Concentration Increase in Flue Gas Across a Wet Scrubber. *Environ. Sci. Technol.* **2003**, 37, 5763-5766.
 55. DeBerry, D., Blythe, G., Pletcher, S., Rhudy, R. "Bench-scale Kinetics Study of Mercury Reductions in FGD Liquors." Presented at DOE/EPA/EPRI Mega-Symposium, Baltimore, MD, 2006.
 56. Ghorishi, B., Downs, B., Renniger, S. *Role of Sulfides in the Sequestration of Mercury by Wet Scrubbers*. Presented to: EPRI-DOE-EPA-AWMA Combined Power Plant Air Pollutant Control Mega Symposium. Baltimore, Maryland. August 28-31, 2006.
 57. Dombrowski, K., McDowell S., Berry, M., Sibley, A., Chang, R., Vosteen, B. *The Balance-of-Plant Impacts of Calcium Bromide Injection as a Mercury Oxidation Technology in Power Plants*. Paper # 27 A&WMA Mega Symposium, Baltimore, MD, August 25–28, 2008.
 58. Linak, W., Ryan, J., Ghorishi, B., Wendt, J. Issues Related to Solution Chemistry in Mercury Sampling Impingers. *J. Air Waste Manag. Assoc.* **2001**, 51 (5), 688-698.

59. Blythe, G., Rhudy, R., Lani, B. W. *Pilot- Scale Testing of Mercury Oxidation Catalysts for Enhanced Control by Wet FGD*. in: Proceedings of the Air Quality V; Mercury, Trace Elements, SO₃, and Particulate Matter Conference; Arlington, VA, Sept 19-21, 2005.
60. Niksa, S., Helble, J., Fujiwara, N. *Interpreting Laboratory Test Data on Homogeneous Mercury Oxidation in Coal-Derived Exhausts*. in: Proceedings of the 94th Annual Air & Waste Management Association Conference, Orlando, FL, June, **2001**.
61. Wilcox, J., Robles, J., Marsden, D., Blowers, P. Theoretically Predicted Rate Constants for Mercury Oxidation by Hydrogen Chloride in Coal Combustion Flue Gases. *Environ. Sci. Technol.* **2003**, 37, 4199-4204.
62. Xu, M., Qiao, Y., Zheng, C., Li, L., Liu, J. Modeling of Homogeneous Mercury Speciation Using Detailed Chemical Kinetics. *Combust. Flame* **2003**, 132, 208–218.
63. Widmer, N., West, J. *Thermochemical Study of Mercury Oxidation in Utility Boiler Fuel Gases*. 93rd Annual Meeting of the Air & Waste Management Association, Salt Lake City, UT, June, 2000.
64. Qiu, J., Sterling, R., Helble, J. *Development of an Improved Model for Determining the Effects of SO₂ on Homogeneous Mercury Oxidation*. In Proceedings of the 28th International Technical Conference on Coal Utilization & Fuel Systems, Clearwater, FL, March, 2003.
65. Niksa, S., Padak, B., Krishnakumar, B., Naik, C. Process Chemistry of Br Addition to Utility Flue Gas for Hg Emissions Control. *Energy Fuels*, **2010**, 24, 1020-1029.
66. Niksa, S., Naik, C., Berry, M., Monroe, L. Interpreting Enhanced Hg Oxidation with Br Addition at Plant Miller. *Fuel Process. Technol.* **2009**, 90, 1372-1377.
67. Bozzelli, J. New Jersey Institute of Technology, Personal Communication, 2009-2010.
68. Donohoue, D., Bauer, D., Cossairt, B., Hynes, A. Temperature and Pressure Dependent Rate Coefficients for the Reaction of Hg with Br and the Reaction of Br with Br: A Pulsed Laser Photolysis-Pulsed Laser Induced Fluorescence Study. *J. Phys. Chem. A*, **2006**, 110, 6623-6632.
69. Zhao, Y., Mann, M., Olson, E., Pavlish, J., Dunham, G. Effects of Sulfur Dioxide and Nitric Oxide on Mercury Oxidation and Reduction Under Homogeneous Conditions. *J. Air Waste Manage. Assoc.* **2006**, 56, 628–635.

70. Presto, A., Granite, E.; *Impact of Sulfur Oxides on Mercury Capture by Activated Carbon*: DOE/NETL 2007 Mercury Control Conference Pittsburgh, PA. December 12, 2007.
71. Bhardwaj, R., *Mercury Uptake and Oxidation Catalyzed by Carbonaceous Surfaces: Impact of Surface Area, Flue gas Constituents and Temperature*. AIChE Annual Meeting, Salt Lake City, UT. 2008.
72. Miller, S., Dunham, G., Olson, E., Brown, T. Flue Gas Effects on Carbon-Based Mercury Sorbent. *Fuel Process. Technol.* **2000**, 65-66, 343-363.
73. Lui, W., Vidic, R. Impact of Flue Gas Conditions on Mercury Uptake by Sulfur-Impregnated Activated Carbon. *Environ. Sci. Technol.* **2000**, 34, 154-159.
74. Olson, E., Laumb, J., Benson, S., Dunham, G., Sharma, R., Miller, J., Pavlish, J. The Multiple Site Model for Flue-gas Mercury Interactions on Activated Carbons: the Basic Site. *Fuel Chem. Div. Prep.* **2003**, 48(1), 30-31.
75. Galbreath, K., Zygarlicke, C., Olson, E., Pavlish, J., Toman, D. Evaluating Mercury Transformation Mechanisms in a Laboratory-Scale Combustion System. *Sci. Total Environ* **2000**, 261, 149-155.
76. Olson, E., Dunham, G., Sharma, R., Miller, S. *Mechanisms of Mercury Capture and Breakthrough on Activated Carbon Sorbents*. Symposia Preprint, American Chemical Society—Division of Fuel Chemistry, 220th ACS National Meeting, vol. 45, No. 4, Aug. 20-23, 2000.

CHAPTER 2

OBJECTIVES

General Objective

The main objective of this study was to determine the extents of elemental mercury oxidation in presence of various flue gas components such as chlorine, bromine, SO₂, and NO_x using two different temperature profiles in the experimental system. The simulated flue gas is obtained by either air-firing or oxy-firing of methane. A related objective is to determine the effects of sample conditioning chemistry on apparent levels of oxidation. The results will be used to support accurate measurement of mercury species and concentrations. They will further support the removal of elemental mercury from coal-derived flue gas streams and the development of kinetic models to predict full-scale performance.

Specific Objectives

- Determine the optimal conditions for the mercury sample conditioning system to decrease the observed bias in the homogeneous mercury measurements when bromine is present in the system.
- Determine the effect of SO₂ on mercury oxidation by bromine under homogeneous conditions.

- Determine the effect of the simultaneous presence of bromine and chlorine on the homogeneous mercury oxidation under high and low quench temperature profiles.
- Determine levels of mercury oxidation by chlorine, bromine and SO₂ under oxy-fuel conditions.
- Validate a detailed kinetic model for predicting mercury oxidation under homogeneous conditions.

CHAPTER 3

EXPERIMENTAL METHODS

The homogeneous mercury reactor used in this study is a 5-cm OD x 4.7-cm ID quartz tube (132 cm in length) located along the center of a high-temperature Thermcraft heater. The reaction tube extends 79 cm below the heater, is temperature controlled, and has a quartz sampling section at the bottom with a capped end (1). Peak gas temperature in the electrically heated zone was about 1080°C.

A methane-fired, premixed burner made of quartz glass supplied a mixture of combustion gases to the reactor (Figure 3.1). All reactants were introduced through the burner and passed through the flame to create a radical pool representative of combustion systems. The design burner heat input was about 300-W, producing 6 slpm of combustion gases. A PS Analytical Mercury Calibration Gas Generator or “CavKit” was the source of elemental mercury. It works on the principle of diluting a saturated Hg vapor at known temperature. Essentially a low flow rate of air is delivered over the Hg reservoir using a mass flow controller (MFC) at 0-20 ml/min. The gas passing over the reservoir becomes saturated at the reservoir temperature. A dilution gas (0-20 L/min) supplied by a second MFC dilutes the saturated Hg vapor into the concentration range of interest.

The mercury analyzer is a TEKRAN 2537A which uses cold vapor atomic

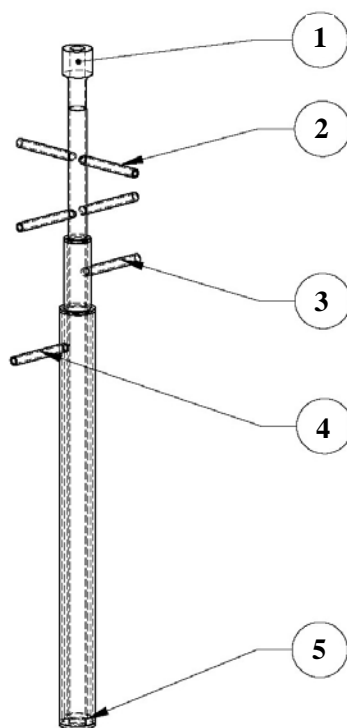


Figure 3.1. Burner configuration, 1 UV Detector Connection (1/2" NPT Threads), 2 Reactant Nozzles (1/4" OD, 4 Typical), 3 Cooling Outlet Nozzle (1/4" OD), 4 Cooling Inlet Nozzle (1/4" OD), 5 Burner Face (1/2" ID). Adapted (1)

fluorescence spectrophotometry (CVAFS) for detection of mercury. The Tekran 2537A features two cartridges. While cartridge A is adsorbing mercury during a sampling period, cartridge B is desorbed and analyzed. The roles of the cartridges are then reversed. This alternate action allows continuous sampling of the inlet stream. The adsorption step uses pure gold as the adsorbent. This material is highly specific to mercury, reducing interferences.

The mercury analyzer is able to measure just elemental mercury. In order to measure total mercury concentrations, the oxidized mercury should be converted to elemental mercury within the system. The conditioning section is designed for this

purpose (Figure 3.2). Two, 2 lpm samples are taken from the reactor. The first stream, representative of total mercury concentrations, is bubbled through an impinger of 2% stannous chloride (SnCl_2) in 3% hydrochloric acid (HCl). In this solution oxidized mercury species, predominantly HgCl_2 , are scrubbed out of the gas, entering the liquid phase of the solution where an oxidation-reduction reaction occurs with the Sn^{2+} . The mercury is then reduced to its elemental form and the tin is further oxidized. The HCl in the solution prevents precipitation of the stannous chloride. The total mercury stream is then bubbled through a second impinger of 5% sodium hydroxide (NaOH) solution to scrub acid gases from the sample stream.

The second sample stream pulled from the reactor is representative of elemental mercury concentrations. This stream is first contacted with an aqueous, 10% potassium chloride (KCl) solution where the oxidized mercury species are scrubbed out of the gas. Hg^{2+} is retained in this solution as a complex with Cl^- ions. Elemental mercury has limited solubility in water and passes through the impinger without being significantly absorbed. The mercury in this stream is now representative of the elemental mercury concentrations in the reactor. This sample stream also passes through a second impinger of 5% sodium hydroxide (NaOH) solution to scrub acid gases.

Both sides of the conditioning system, the total and the elemental side, were modified in this study to avoid bias in mercury measurements observed when bromine and SO_2 were present in the system. The details of the modifications considered will be cited in Chapter 5 and Appendix A. It was concluded that the optimal configuration of the conditioning system is:

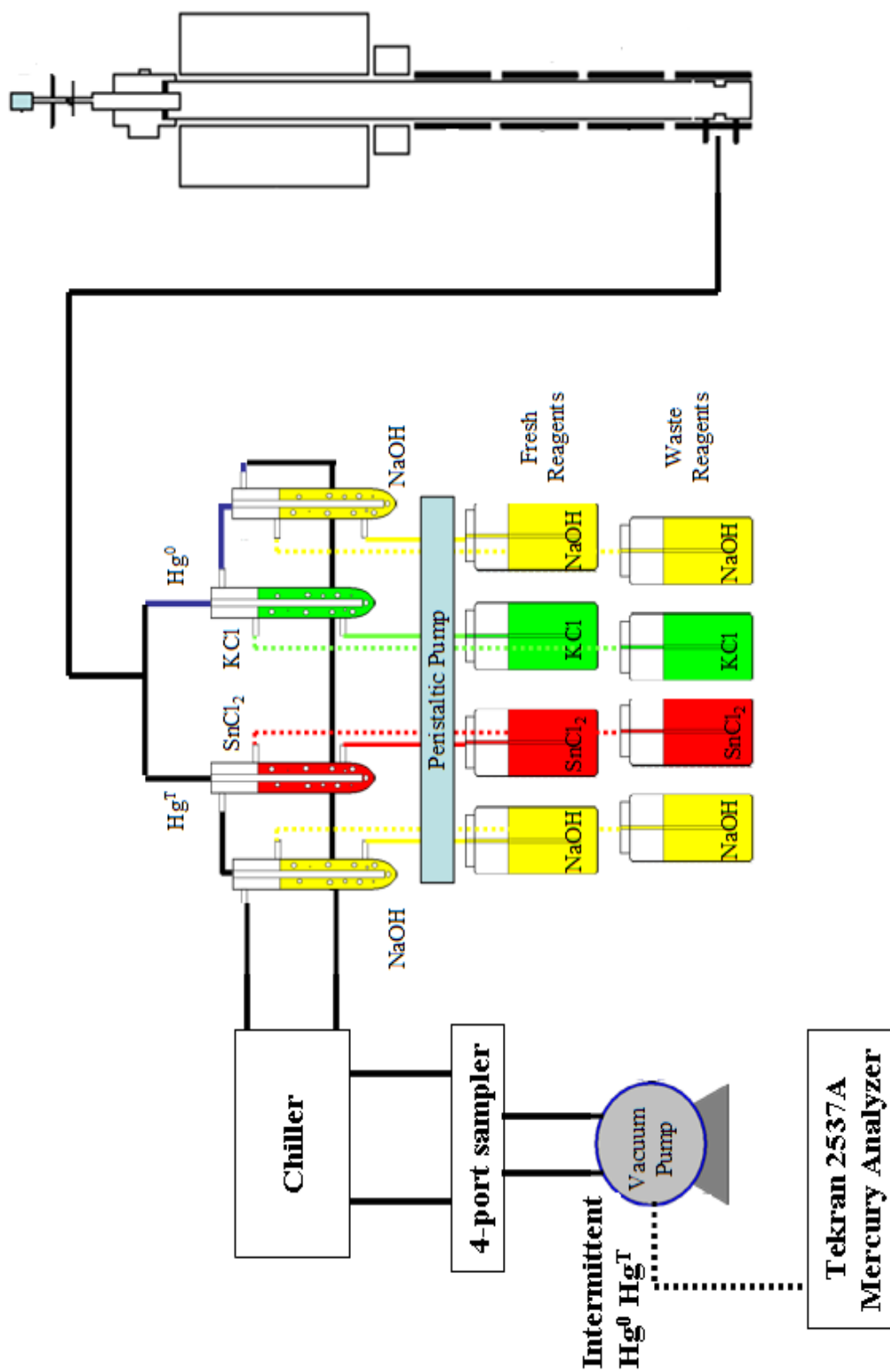


Figure 3.2. Mercury Analysis System. Adapted (1)

- Total side of the conditioning system (In presence of bromine) Impinger 1: Solution of 4 wt % $\text{NH}_2\text{OH}\cdot\text{HCl}$ (hydroxylamine hydrochloride) and 20 wt % NaOH .
- Elemental side of the conditioning system (For the case when both bromine and SO_2 are present in the system):
Impinger 1: Solution of 5 wt % NaOH .
Impinger 2: Solution of 10 wt % KCl and 0.5 wt % $\text{Na}_2\text{S}_2\text{O}_3$ (sodium thiosulfate).
Impinger 3: Solution of 5 wt % NaOH .

The mercury analyzer uses gold traps to collect elemental mercury which is subsequently desorbed into a measurement cell. Measurements in the mercury analyzer can be affected by the presence of acid gases such as HCl and SO_2 , and the blockages that can arise from the fact that the water from the combustion of methane with air can condense in the cold spots along the system. For these reasons it is necessary to remove water and acid gases before they reach the mercury analyzer. As mentioned before, the acid gases are removed by the NaOH impingers installed on each side of the conditioning system. To remove the water, the two sample streams are sent through a Universal Analyzer Model 540 chiller to reduce the dew point of the samples to 4°C . The heat exchangers on the chiller are constructed of Kynar and glass. Upstream of the chiller, each sample stream is passed through a Pall Gelman 0.2 micron, PFA filter.

The overall configuration of the burner, reactor, mercury source and mercury analysis system is shown in Figure 3.3. This figure also shows the system for injecting the halogens considered in this study as well as the methane for the flame.

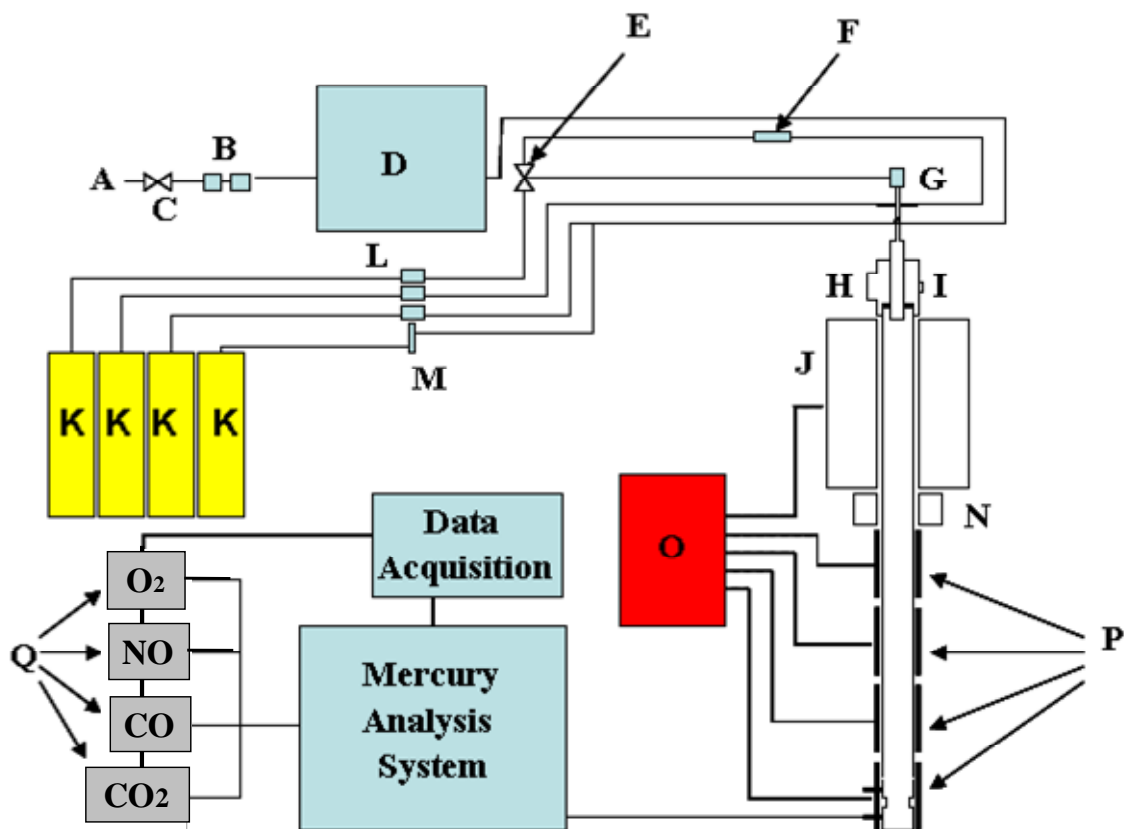


Figure 3.3. Mercury reactor configuration. Adapted (1)

A: Compressed air, B: Filter, C: Pressure regulator, D: Mercury cal gas generator (CavKit), E: Solenoid valve, F: Flashback arrestor, G: UV valve, H: Support T and blow off nozzle, I: Purge nozzle, J: Thermcraft heater, K: Gas cylinders, L: Mass flow controllers, M: Rotameter, N: Inswool, O: Temperature controllers, P: Heating tapes, Q: Analyzers.

The tubular reactor was operated under laminar (maximum Reynolds number ~ 188) flow conditions with two temperature profiles along the reactor, shown in Figure 3.4, a high-quench profile (440 K/s) and a low-quench profile (220 K/s). Temperature and concentration changes in the radial direction were considered to be negligible. Fry (1) verified this assumption in the same reactor by predictions of the Peclet number along the quartz tube. His results indicated that axial dispersion due to molecular diffusion can result in an essential flat radial profile. Therefore, the reactor can be considered as plug-flow where there is no mixing in the axial direction but perfect mixing in the radial direction. With this approximation, it is viable to assume that the radial gradients in either concentration or temperature are negligible relative to the corresponding gradients along the reactor (2, 3).

The inlet mercury concentration was $25 \mu\text{g}/\text{m}^3$ and the concentration of other gas-phase species are provided in Chapters 5, 6 and 7. For each test, a mercury mass balance was closed in order to verify that the amount of mercury leaving the source was the same as that detected by the analyzer. Figure 3.5 shows the output from a typical mass balance experiment. After lighting the burner, the mass balance was checked again and additional flue gases were added through the burner and the mercury oxidation was determined as the difference between the total mercury stream and the elemental mercury stream as indicated in Figure 3.5.

For the oxy-fuel experiments, the air for the combustion process was replaced by a mixture 27% O_2 and 73% CO_2 .

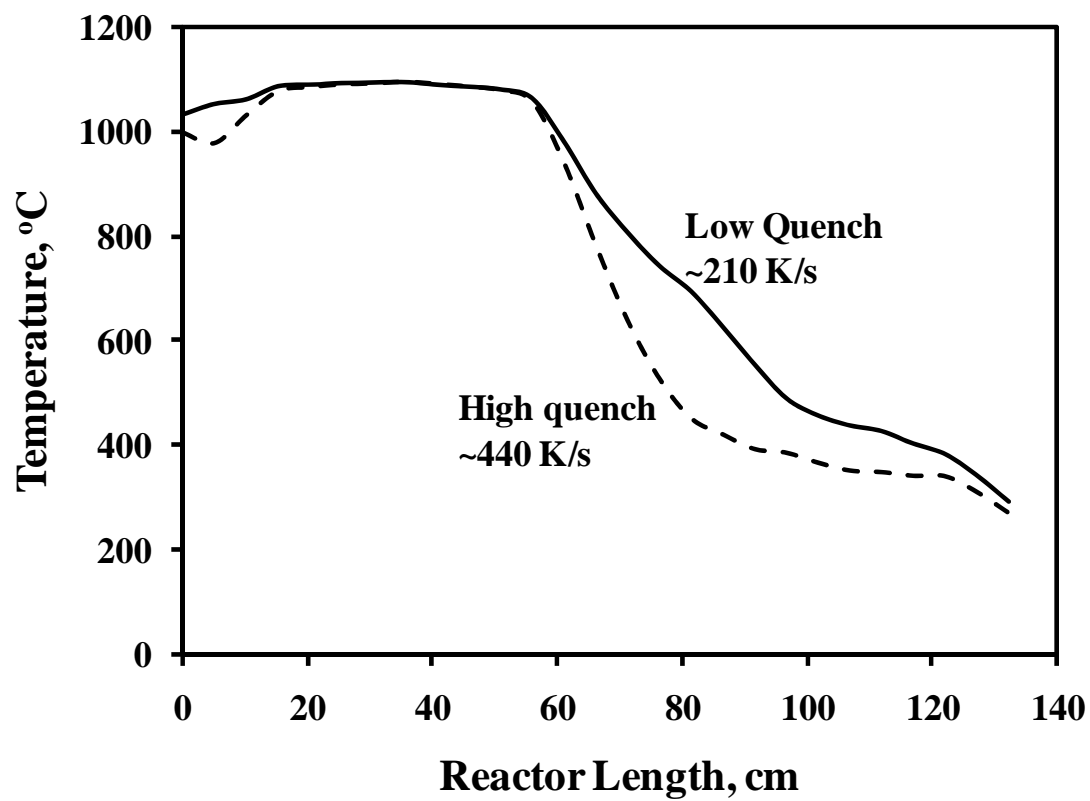


Figure 3.4. Temperature profiles in laboratory furnace.

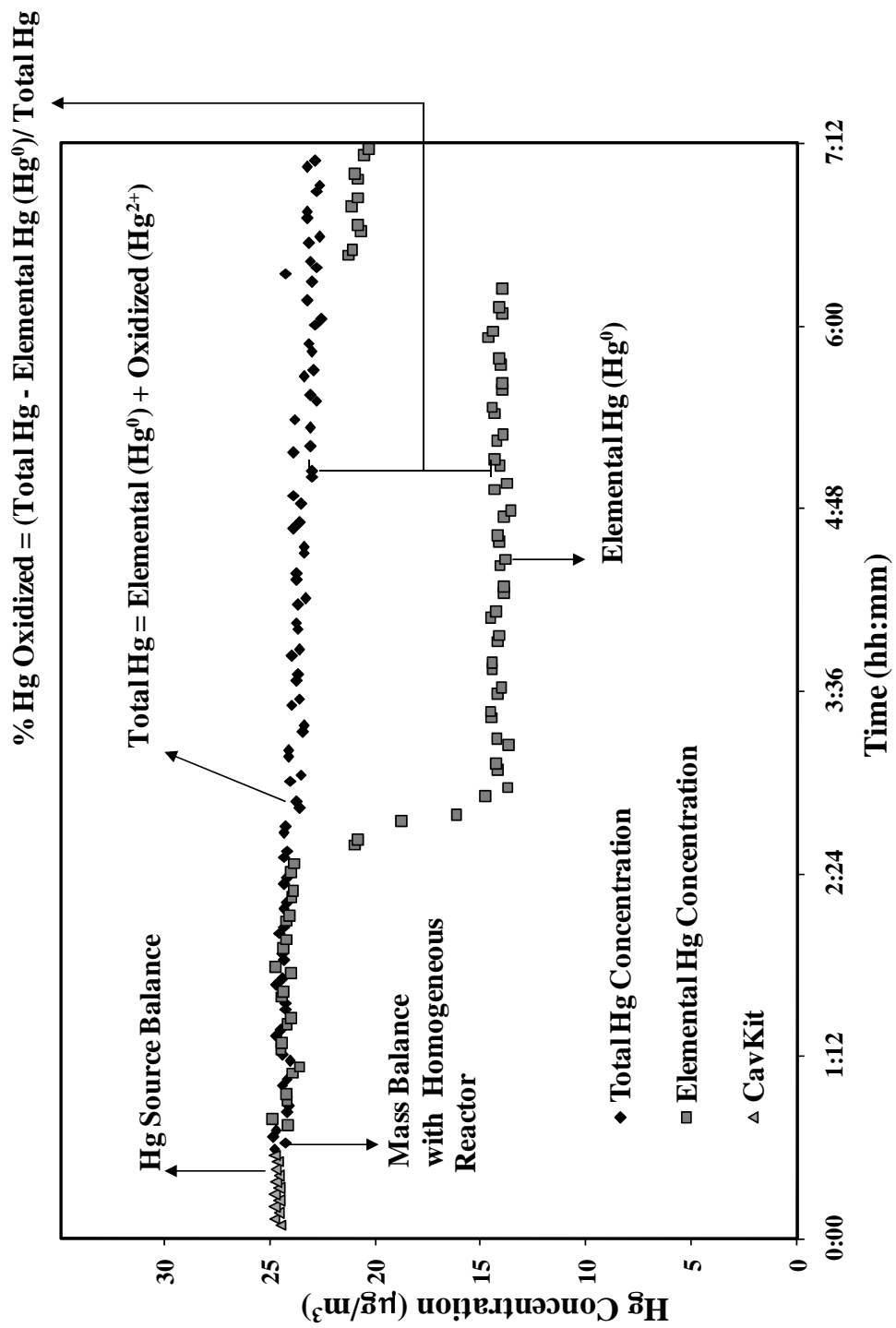


Figure 3.5. Sample of an experimental measurement from the analyzer.

References

1. Fry, A. Experimental and Kinetic Modeling Investigation of Gas-Phase Mercury Oxidation Reactions with Chlorine. Ph.D. Thesis, University of Utah, 2008.
2. Fogler S. H., *Elements of Chemical Reaction Engineering*; Fourth ed., Prentice Hall PTR., 2006.
3. CHEMKIN 4.1, Reaction Design, Theory Manual.

CHAPTER 4

HOMOGENEOUS MERCURY OXIDATION MODEL

CHEMKIN 4.1 was used as the computational platform to simulate the homogeneous mercury oxidation under different temperature profiles and compositions of the flue gas.

As described in the previous section, the reaction system used for this study consists of a burner that generates combustion products and a homogeneous reactor that is temperature controlled. This configuration allows the study of reactions between mercury and different flue gas components. To simulate the methane-fired burner, a perfectly stirred reactor (PSR) was used. The kinetic mechanism and thermodynamic inputs for this reactor were specified by the GRI mechanism incorporated in the CHEMKIN 4.1 software. The input parameters as well as the gas composition obtained are presented in Appendix B.

The combustion products generated in the burner were the input for the homogeneous reactor that was represented by a plug-flow reactor (PFR). The parameters for the PFR were matched to the experimental conditions and included volumetric flows, dimensions, mercury and halogen inlet concentrations, pressure, and temperature profiles. The reaction mechanism was developed by Reaction Engineering international (REI) and included hydrocarbon chemistry and submodels for Hg, chlorine, bromine, SO_x and NO_x

chemistry (1-21). A schematic representation of the homogeneous reactor used for the CHEMKIN 4.1 simulations is shown in Figure 4.1.

The experimental data (24) were compared to five Hg-Cl and three Hg-Br kinetic mechanisms available in the literature (4, 9, 11, 12, 16, 18, 22, 23). The different mercury-halogen kinetic sets were combined with the Reaction Engineering International (REI) halogen kinetic set and submechanisms for NO_x, SO_x, and hydrocarbon chemistry in order to accurately model the conditions of the experiments. The halogen detailed kinetic set used in the REI mechanism includes reactions from several sources. The chlorine mechanism consists of Cl reactions from Roesler et al. (12), additional NO-Cl reactions from Niksa et al. (10, 11) and Bozzelli (25), and C_xH_y-Cl reactions from Bozzelli. The bromine kinetic set contains reactions from the NIST Halogen mechanism (23) and several additional reactions with NO_x, Cl, and OH from Bozzelli (25). Two experimental temperature profiles, high quench (HQ, 440 K/s) and low quench (LQ, 210 K/s) were used for the modeling. Both time-temperature histories were used with the Hg-Cl and Hg-Br kinetic sets. The mercury-halogen kinetic sets that come closest to being able to describe the experimental data are Xu et al. (21) for Hg-Cl and Bozzelli (25) for Hg-Br. These kinetic mechanisms are shown in Tables 4.1 and 4.2. The kinetic parameters shown are for use with the modified Arrhenius rate equation:

$$k = AT^n \exp(-E_a/RT) \quad (4.1)$$

The Hg-Cl mechanism used by Xu et al. (21) contains eight reactions from Widmer et al. (2) and four additional reactions with novel kinetics.

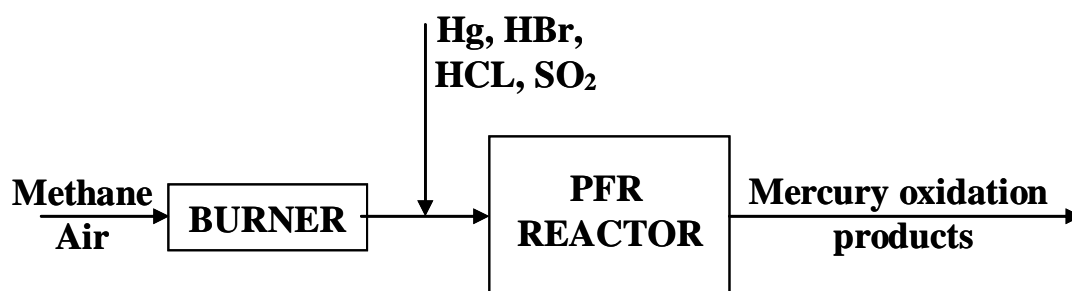


Figure 4.1. Schematic representation of the homogeneous reactor for the CHEMKIN 4.1 model.

Table 4.1. Xu et al. 2003 Hg-Cl kinetic mechanism. Adapted (21)

Reaction	A (mol-cm-s-K)	n	Ea (cal/mol)
$\text{Hg} + \text{Cl} + \text{M} = \text{HgCl} + \text{M}$	240000000	1.4	-14400
$\text{Hg} + \text{Cl}_2 = \text{HgCl} + \text{Cl}$	1.39E+14	0	34000
$\text{Hg} + \text{HOCl} = \text{HgCl} + \text{OH}$	4.27E+13	0	19000
$\text{Hg} + \text{HCl} = \text{HgCl} + \text{H}$	4.94E+14	0	79300
$\text{HgCl} + \text{Cl}_2 = \text{HgCl}_2 + \text{Cl}$	1.39E+14	0	1000
$\text{HgCl} + \text{HCl} = \text{HgCl}_2 + \text{H}$	4.94E+14	0	21500
$\text{HgCl} + \text{Cl} + \text{M} = \text{HgCl}_2 + \text{M}$	2.19E+18	0	3100
$\text{HgCl} + \text{HOCl} = \text{HgCl}_2 + \text{OH}$	4.27E+13	0	1000
$\text{Hg} + \text{ClO} = \text{HgO} + \text{Cl}$	1.38E+12	0	8320
$\text{HgO} + \text{HCl} = \text{HgCl} + \text{OH}$	96300	0	8920
$\text{HgO} + \text{HOCl} = \text{HgCl} + \text{HO}_2$	4.11E+13	0	60470
$\text{Hg} + \text{ClO}_2 = \text{HgO} + \text{ClO}$	18700000	0	51270

Table 4.2 Bozzelli 2010 Hg-Br kinetic mechanism. Adapted (25)

Reaction	A (mol-cm-s-K)	n	Ea (cal/mol)
$\text{Hg} + \text{Br} \rightleftharpoons \text{HgBr}$	5.2E+18	-2.86	461
$\text{Hg} + \text{Br}_2 = \text{HgBr} + \text{Br}$	9.94E+20	-2.42	28933
$\text{HgBr} + \text{H} \rightleftharpoons \text{Hg} + \text{HBr}$	2.7E+13	0	2300
$\text{HgBr} + \text{OH} \rightleftharpoons \text{Hg} + \text{HOBr}$	3.27E+12	0	1000
$\text{HgBr} + \text{Br}_2 \rightleftharpoons \text{HgBr}_2 + \text{Br}$	7.39E+12	0	1000
$\text{HgBr} + \text{Br} \rightleftharpoons \text{HgBr}_2$	3.8E+24	-4.17	1974
$\text{HgBr}_2 + \text{H} \rightleftharpoons \text{HgBr} + \text{HBr}$	4640	2.5	1910
$\text{HgBr} + \text{HOBr} \rightleftharpoons \text{HgBr}_2 + \text{OH}$	2.27E+12	0	1700
$\text{HgBr} + \text{Cl}_2 = \text{HgBrCl} + \text{Cl}$	6.7E+12	0	1250
$\text{HgBr} + \text{BrO} = \text{HgBr}_2 + \text{O}$	2.25E+12	0	1150
$\text{HgBr} + \text{O} = \text{BrO} + \text{Hg}$	3.35E+13	0	1300
$\text{HgCl} + \text{Br}_2 = \text{HgBrCl} + \text{Br}$	8.2E+11	0	1050
$\text{HgOH} + \text{Br} \rightleftharpoons \text{HgBrOH}$	1.57E+30	-7.28	1903
$\text{HgOH} + \text{Br} \rightleftharpoons \text{HgBr} + \text{OH}$	6.67E+13	-0.36	218
$\text{HgBr} + \text{OH} \rightleftharpoons \text{HgBrOH}$	2.19E+29	-5.77	2976
$\text{HgO} + \text{Br} \rightleftharpoons \text{HgBrO}$	8.29E+24	-4.75	1735
$\text{HgBrOH} + \text{OH} = \text{HgBrO} + \text{H}_2\text{O}$	2.45E+12	0	850
$\text{HgBrO} + \text{HO}_2 = \text{HgBrOH} + \text{O}_2$	5.5E+11	0	0
$\text{Hg} + \text{Br}_2 = \text{HgBr}_2$	1.19E+11	-0.01	4736

To simulate the effect of the simultaneous presence of bromine and chlorine on mercury oxidation, the kinetic mechanism developed by Joe Bozzelli was used with the parameters showed in Table 4.3. This bromine-chlorine mechanism was added to the mercury bromine and mercury-chlorine mechanisms previously described.

The model was compared to experimental data for air-firing conditions, high and low-quench temperature profiles and different compositions of the simulated flue gas.

Table 4.3 Bozzelli Mechanism for the bromine-chlorine interactions. Adapted (25)

Reaction	A (mol-cm-s-K)	n	E_a (cal/mol)
Cl + ClBr = Cl ₂ + Br	5.50E+12	0	1000
Br + ClBr = Br ₂ + Cl	3.35E+12	0	8900
Cl + Br + M = ClBr + M	3.90E+14	0	0
Br + NO + M = BrNO + M	9.50E+14	-0.175	0
Br + BrNO = Br ₂ + NO	5.00E+12	0	0
Cl + BrNO = ClBr + NO	1.00E+13	0	1000
OH + BrNO = BrOH + NO	5.50E+12	0	740
Br + NO ₂ + M = BrNO ₂ + M	1.50E+17	0	0
BrR + BrNO ₂ = Br ₂ + NO ₂	5.50E+12	0	1200
Cl + BrNO ₂ = ClBr + NO ₂	8.50E+12	0	900

References

1. Hall, B.; Schager, P.; Lindquist, O. Chemical Reactions of Mercury in Combustion Flue Gases. *Water, Air, Soil Poll.* **1991**, 56, 3-14.
2. Widmer, N.; Cole, J.; Seeker, W.; Gaspar, J. A. Practical Limitation of Mercury Speciation in Simulated Municipal Waste Incinerator Flue Gas. *Combust. Sci. and Tech.* **1998**, 134, 315-326.
3. Widmer, N.; West, J.; Cole, J. *Thermochemical Study of Mercury Oxidation in Utility Boiler Flue Gases*. Proceedings of the A&WMA Annual Conference, Salt Lake City, UT, June, 2000.
4. Ghorishi, S. *Fundamentals of Mercury Speciation and Control in Coal-fired Boilers*. EPA-600/R-98-014, February 1998.
5. Laudal, D.; Brown, T.; Nott, B. Effects of Flue Gas Constituents on Mercury Speciation. *Fuel Process. Technol.* **2000**, 65-66, 157-165.
6. Sliger, R.; Kramlich, J.; Marinov, N. Towards the Development of a Chemical Kinetic Model for the Homogeneous Oxidation of Mercury by Chlorine Species. *Fuel Process. Technol.* **2000**, 65-66, 423-438.
7. Mamani-Paco, R.; Helble, J. *Bench-scale Examination of Mercury Oxidation Under Non-isothermal Conditions*. Proceedings A&WMA Annual Conference, Salt Lake City, UT, June, 2000.
8. Qiu, J.; Sterling, R.; Helble, J. *Development of an Improved Model for Determining the Effects of SO₂ on Homogeneous Mercury Oxidation*. Proceedings of the 28th International Technical Conference on Coal Utilization & Fuel Systems, Clearwater, FL, March, 2003.
9. Fry, A.; Cauch, B.; Silcox, G.; Lighty, J.; Senior, C. *Experimental Evaluation of the Effects of Quench Rate and Quartz Surface Area on Homogeneous Mercury Oxidation*. in: 31st International Symposium on Combustion, Heidelberg, Germany, August, 2006.
10. Niksa, S.; Helble, J.; Fujiwara, N. Kinetic Modeling of Homogeneous Mercury Oxidation: the Importance of NO and H₂O in Predicting Oxidation in Coal-derived Systems. *Environ. Sci. Technol.* **2001**, 35 (18), 3701-3706.
11. Niksa, S.; Helble, J.; Fujiwara, N. *Interpreting Laboratory Test Data on Homogeneous Mercury Oxidation in Coal-derived Exhausts*. Proceedings of the 94th Annual Air & Waste Management Association Conference, Orlando, FL, June 2001.

12. Roesler, J.; Yetter, R.; Dryer, F. Detailed Kinetic Modeling of Moist CO Oxidation Inhibited by Trace Quantities of HCl. *Combust. Sci. and Tech.* **1992**, 85, 1-22.
13. Roesler, J.; Yetter, R.; Dryer, F. Kinetic Interactions of CO, NO_x, and HCl Emissions in Post Combustion Gases. *Combust. Flame* **1995**, 100, 495-504.
14. Senior, C.; Lignell, D.; Chen, Z.; Shiley, B.; Sarofim, A. *Modeling Gaseous Mercury Behavior in Practical Combustion Systems*. Proceedings of the International Conference on Air Quality IV, Arlington, VA, September 22-24, 2003.
15. Sable, S.; de Jong, W.; Spliethoff, H. Combined Homo- and Heterogeneous Model for Mercury Speciation in Pulverized Fuel Combustion Flue Gases. *Energy Fuels* **2008**, 22 (1), 321-330.
16. Wilcox, J.; Marsden, D.; Blowers, P. Evaluation of Basis Sets and Theoretical Methods for Estimating Rate Constants of Mercury Oxidation Reactions Involving Chlorine. *Fuel Processing Technology* **2004**, 85 (5), 391-400.
17. Wilcox, J.; Robles, J.; Marsden, D.; Blowers, P. Theoretically Predicted Rate Constants for Mercury Oxidation by Hydrogen Chloride in Coal Combustion Flue Gases. *Environ. Sci. Technol.* **2003**, 37 (18), 4199-4204.
18. Krishnakumar, B.; Helble, J. Understanding Mercury Transformations in Coal-Fired Power Plants: Evaluation of Homogeneous Hg Oxidation Mechanisms. *Environ. Sci. Technol.* **2007**, 41 (22), 7870-7875.
19. Edwards, J.; Srivastava, R.; Kilgroe, J. A Study of Gas-phase Mercury Speciation Using Detailed Chemical Kinetics. *J. of the Air & Waste Manag. Assoc.* **2001**, 51, 869-877.
20. Senkan, S. *Survey of Rate Coefficients in the C-H-Cl-O System*. In *Gas-Phase Combustion Chemistry*; Gardiner, W. C., Jr.; Springer-Verlag: New York, 2000; 389-487.
21. Xu, M.; Qiao, Y.; Zheng, C.; Li, L.; Liu, J. Modeling of Homogeneous Mercury Speciation Using Detailed Chemical Kinetics. *Combust. Flame* **2003**, 132, 208-218.
22. Niksa, S.; Padak, B.; Krishnakumar, B.; Naik, C., Process Chemistry of Br Addition to Utility Flue Gas for Hg Emissions Control. *Energy Fuels* **2010**, 24 (2), 1020-1029.

23. N.I.S.T., <http://kinetics.nist.gov/kinetics/index.jsp> 2006.
24. Cauch, B., Silcox, G., Lighty, J., Wendt, J., Fry, A., Senior, C. Confounding Effects of Aqueous-Phase Impinger Chemistry on Apparent Oxidation of Mercury in Flue Gases. *Environ. Sci. Technol.* **2008**, 42, 2594–2599.
25. Bozzelli, J. New Jersey Institute of Technology, Personal Communication, 2009-2010.

CHAPTER 5

GAS-PHASE MERCURY OXIDATION BY BROMINE:

EFFECTS OF IMPINGER-BASED MERCURY

SPECIATION METHODS

Abstract

In the presence of bromine, a bias in the total (elemental plus oxidized) mercury concentration measured using a mercury continuous emission monitor (CEM) was detected when using a wet conditioning system with various reducing agents on the total side. The apparent ability of stannous chloride solution to reduce oxidized mercury to elemental was considerably reduced by the presence of bromine. After testing different configurations on the total side of the conditioning system, it was determined that this apparent bias was considerably reduced when an aqueous mixture of hydroxyl-amine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) and NaOH was used instead of the traditional reductant, stannous chloride (SnCl_2). The simultaneous presence of bromine and SO_2 also resulted in biased elemental levels of mercury. Lower levels of oxidation by bromine were observed in the presence of SO_2 . These observations may be due to the ability of SO_2 to act as a reductant and prevent the oxidation of elemental mercury on both the total and elemental sides of the conditioning system. The performance of wet conditioning systems may be improved by the addition of a reducing agent, like sodium thiosulfate, to the sodium hydroxide impingers that are part of most wet systems. Bubbling bromine

through aqueous sodium hydroxide solutions is known to result in the formation of hypobromites and bromates, both of which are powerful oxidants that are destroyed by reductants like SO_2 and sodium thiosulfate.

Introduction

The adverse impacts of mercury on human health and the environment, along with regulations to decrease its emissions have made it the focus of many scientific investigations (1-7). Proposed methods for reducing emissions from coal-fired power plants, one of the major sources of anthropogenic mercury, are dependent on mercury speciation. Three main forms of mercury are present in the flue gas from burning coal, elemental (Hg^0), oxidized (Hg^{2+}) and particulate-bound (Hg^p). Elemental mercury is more difficult to capture and is largely emitted to the atmosphere while the total and particulate bound forms can be efficiently removed by existing pollutant control devices. The task is then to find methods that allow increasing the extent of either oxidized or particulate-bound mercury in flue gas.

The concentration of elemental mercury in flue gas is conveniently measured using cold vapor atomic fluorescence spectrophotometry (CVAFS) (8-11). Application of this technique to oxidized mercury species requires their reduction to the elemental state. The reduction process is commonly performed by continuous flow, wet conditioning systems. Wet systems provide semicontinuous mercury measurements with the inconveniences of having to prepare aqueous solutions of various reagents and suffer from various interferences. Linak et al. (12) studied the effect of chlorine on mercury oxidation using two different wet conditioning systems the Ontario Hydro (OH) and the Alkaline Mercury Speciation methods. They observed a bias of about 10-20% in

elemental mercury for chlorine concentrations as low as 1 ppm in the simulated flue gas mixture. It was suggested by the authors that this deviation was generated from liquid-phase interactions occurring inside the liquid-phase solutions of the conditioning system rather than gas-phase interactions. It was probable that the hypochlorite ion (OCl^-) in the potassium chloride impinger was oxidizing some of the elemental mercury leading to a false increase in the extent of mercury oxidation. This deviation in mercury measurements was mitigated by the addition of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) to the potassium chloride solution. This component reacts with OCl^- reducing its concentration in the solution and thus decreasing its possibility of oxidizing the elemental mercury.

This bias in elemental mercury measurements when chlorine is present in the system was also observed by previous studies performed under our experimental conditions (13). Based on the experimental observations it was determined that the addition of 0.5 wt % $\text{Na}_2\text{S}_2\text{O}_3$ to the 10 wt % KCl solution was enough to mitigate the bias.

Wet conditioning systems are based on the ability of the impinger solutions to reduce or retain the oxidized mercury in order to allow just the elemental mercury to reach the analyzer. In the presence of bromine, the efficiency of these systems can be considerably reduced (14-17). Although pH adjustments, elimination of cold spots, eradication of flue gas contact with metallic surfaces and the use of dry methods have been suggested as potential ways to improve mercury speciation measurements, little has been reported on improving wet conditioning systems.

The objective of this study is to determine the effects of various impinger solutions on the effectiveness of wet conditioning systems for application to mercury

speciation in the presence of bromine. For total mercury measurements, the ability of the stannous chloride solution to reduce oxidized mercury was studied. The confusing effects of sulfur dioxide on levels of oxidized mercury were also examined. Different compositions of the impinger solutions and configurations on both sides of the conditioning system were tested. The results obtained from this investigation are unique and are useful for the improvement of mercury measurements by wet conditioning systems and consequently to the development of more efficient methods for mercury emissions mitigation.

Experimental

The reactor used in this study is a 50-mm OD x 47-mm ID quartz tube (132 cm in length) located along the center of a high-temperature Thermcraft heater. The tube extends 79 cm below the heater, is temperature controlled, and has a quartz sampling section at the bottom with a capped end (18). The peak gas temperature in the electrically heated zone was 1080°C.

A methane-fired, premixed burner made of quartz glass supplied realistic combustion gasses to the reactor. All reactants were introduced through the burner and passed through the flame to create a radical pool representative of combustion systems. The burner heat input was about 300-W, producing 6 slpm of combustion gases. The source of elemental mercury in the reactor was a PS Analytical Mercury Calibration Gas Generator or “CavKit”.

Two quench rates, representative of industrial conditions and shown in Figure 5.1, were used in these experiments: 440 K/s (high-quench) and 210 K/s (low-quench). The low temperature region (around 350°C), extends over 3 seconds with the high-quench

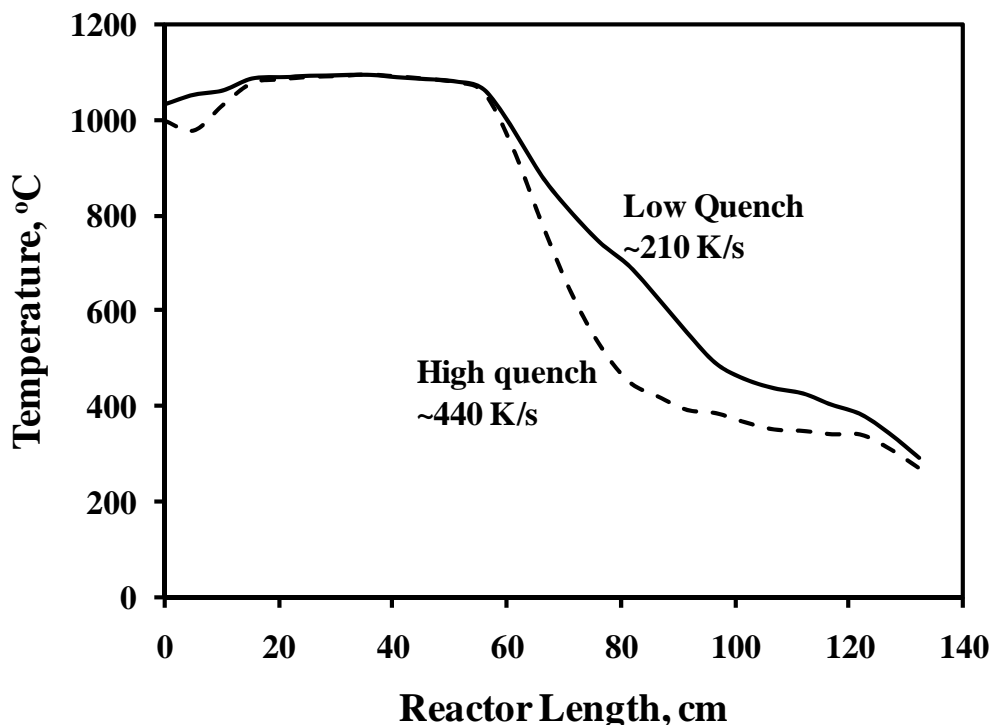


Figure 5.1. Temperature profiles in laboratory furnace.

profile and represents flue-gas temperatures at the end of the convective pass of a boiler. These low temperatures were necessary for mercury oxidation reactions to occur.

For mercury analysis, two sample streams were taken from the bottom of the reaction chamber and introduced into the wet-chemical conditioning system, shown in Figure 5.2. In the baseline conditioning system, one stream was bubbled through an acidic 2% SnCl_2 solution to reduce all mercury to elemental form. This stream was analyzed for the total mercury concentration. The other stream was passed through a solution containing 10 wt% KCl and 0.5 wt% $\text{Na}_2\text{S}_2\text{O}_3$ to capture oxidized mercury. Sodium thiosulfate was added to prevent oxidation of elemental mercury by halogens in solution (8). This stream was analyzed for the elemental mercury concentration. A 5 wt% NaOH solution was used to remove acid gases from each of the sample streams. The

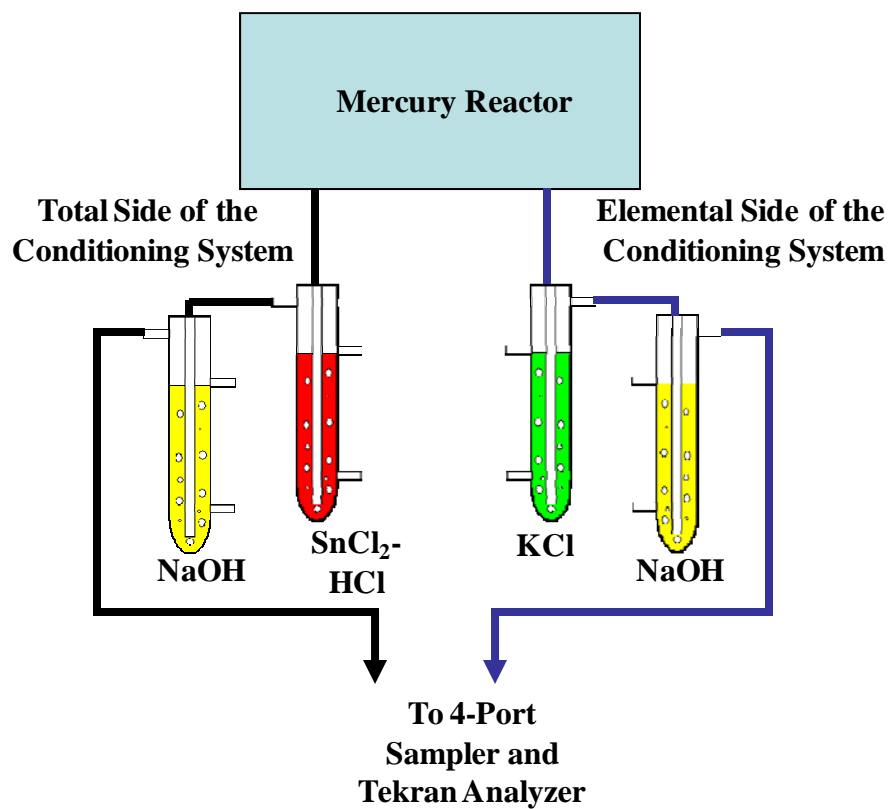


Figure 5.2. Baseline wet-chemical conditioning system.

impingers had a flow-through arrangement on the liquid side, so that they were continually being refreshed. The two sample streams passed through a chiller to remove any water. A Tekran 2537A mercury analyzer was used to measure the elemental mercury concentration of each stream. A four-port sampler controlled which stream the Tekran Analyzer sampled. The concentration of oxidized mercury was calculated from the difference between the total and elemental mercury concentrations.

The major flue gas components are shown in Table 5.1. The gases and vapors entering the reactor passed through the methane fired burner and their concentration was measured using California Analytical Instruments Analyzers ZRH Infrared Gas Analyzer for CO and CO₂, Paramagnetic Oxygen Analyzer Model 100P and NO_x Analyzer Model 300-CLD.

Table 5.1. Flue gas composition for experiments

Species	Concentration
O₂	0.8 vol. %
H₂O	16.5 vol %
CO₂	7.7 vol. %
NO	30- 500 ppm
SO₂*	0 - 500 ppm
HCL**	0 - 500 ppm
HBr***	0 - 50 ppm
Hg⁰	25 g/Nm ³

* Bottle composition 6000 ppm (SO₂) in air.

** Assuming all chlorine added as HCL (bottle composition 6000 ppm Cl₂ in air).

*** Assuming all bromine added as HBr (bottle composition 3000 ppm Br₂ in air).

Results

The performance of the wet conditioning system was evaluated in presence of bromine and SO₂. As shown in Figure 5.3, the presence of bromine decreased the total and elemental mercury concentrations. When both bromine and SO₂ were present, the decrease in the elemental mercury concentration was less. These results suggest that in the absence of SO₂, bromine is oxidizing mercury in the conditioning system. Different configurations of both sides of the conditioning system were tested to determine the optimal conditions to measure mercury speciation in the presence of bromine and SO₂.

Total Side of the Conditioning System

In all experiments, an initial mercury balance was closed that just involved the mercury source and the mercury analyzer. A second balance included the reactor and the burner. In both cases, no halogens or SO₂ were present. Figure 5.3 shows the closure of the initial mercury balances; it was observed that in absence of halogens the total and elemental mercury concentrations are the same. If the effectiveness of the conditioning system were high, it would be expected that in presence of halogens the elemental mercury concentration would decrease while the total mercury concentration would remain unchanged. However, the experimental results in Figure 5.3 show a decrease in total mercury as soon as bromine is present; this decrease is proportional to the bromine concentration and disappears when the bromine is stopped. This reduction in total mercury could be an indication of low efficiency in the conversion of oxidized mercury back to elemental by the stannous chloride solution. It could also be an indication that elemental mercury is being oxidized in the hydroxide impinger. The usual configuration for the total side of the conditioning system was an impinger containing 5 wt % SnCl₂

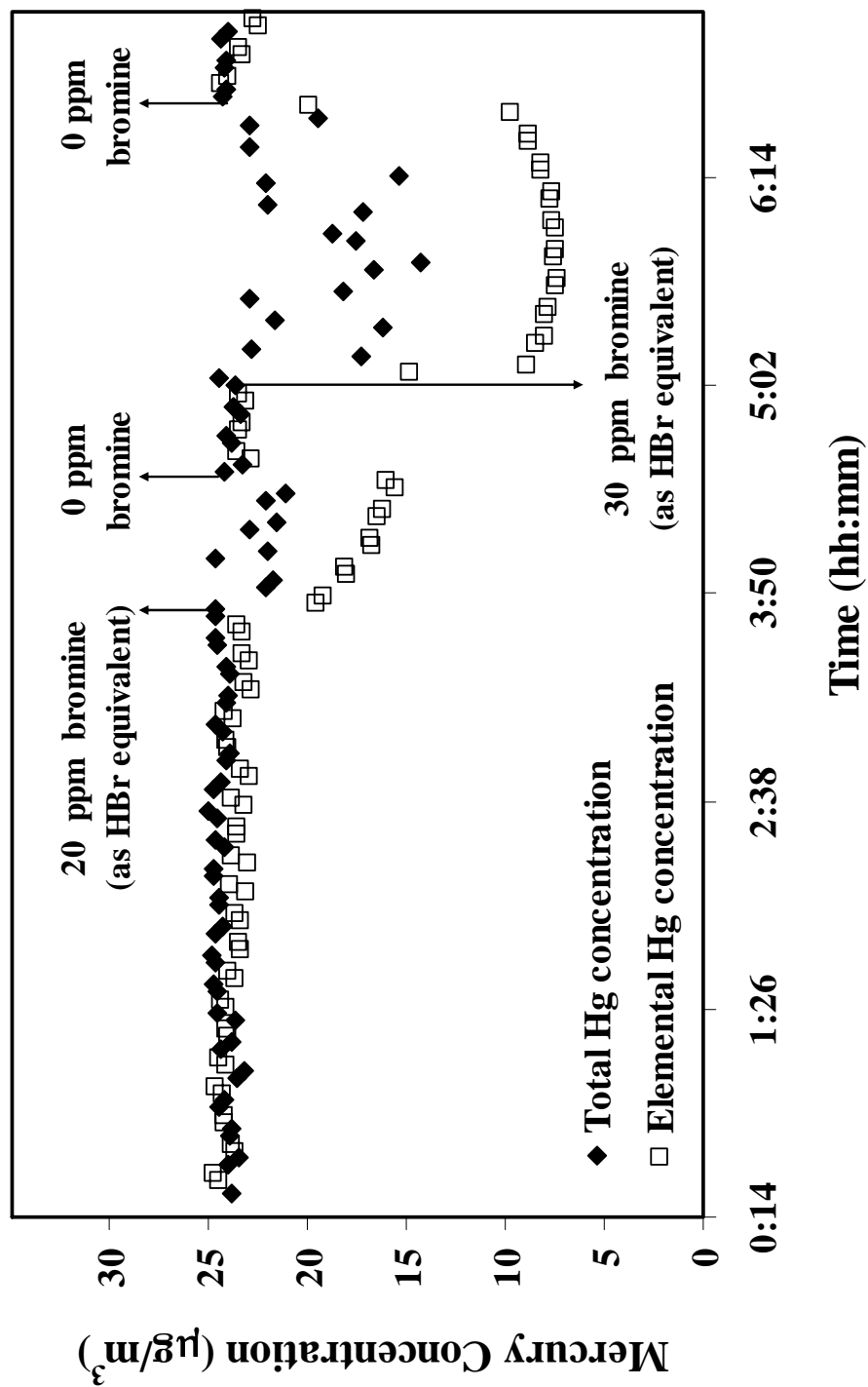


Figure 5.3. Total and elemental mercury concentrations with the addition of 40 and 80 ppm bromine (as HBr equivalent) using the high-quench profile. These results were obtained with the baseline conditioning system shown in Figure 5.2.

and 3 wt % HCl in water, followed by an impinger containing NaOH, as shown in Figure 5.2. To decrease the deviation in total mercury measurements, modifications were made to the total side of the conditioning system: (1) different concentrations and pH's of the stannous chloride solution (Figure 5.4), (2) an additional NaOH impinger upstream of the stannous chloride impinger to remove excess of bromine (Figure 5.5), (3) pretreatment of the flue gas stream with a hydroxylamine hydrochloride solution before the stannous chloride (Figure 5.6), and (4) replacement of the stannous chloride solution by an hydroxylamine hydrochloride- sodium hydroxide solution (Figure 5.6).

Figure 5.4 shows the decrease in total mercury with concentrations of SnCl_2 -HCl ranging from 3 to 10 wt. %. The decreases were calculated using the difference between the total side value and the baseline concentration of $25 \mu\text{g}/\text{m}^3$. No SO_2 was added to the reactor and the concentrations of NO and bromine were 30 ppm and 50 ppm (as HBr equivalent) respectively. Figure 5.4 shows that none of the conditions tested caused a significant improvement in the recovery of total mercury. Using pH values greater than five, which were obtained by adding volumes higher than 40 ml of the 5 wt % NaOH solution, caused precipitation of tin hydroxides. In an ideal conditioning system, there would be no decrease in total mercury.

Figure 5.5 shows the decrease in total mercury when additional NaOH impingers were installed before the SnCl_2 -HCl impinger. It was expected that the additional NaOH impinger would remove Br_2 before it reached the SnCl_2 impinger by the reaction $\text{Br}_2 + 2\text{NaOH} = \text{NaBr} + \text{NaOBr} + \text{H}_2\text{O}$, and possibly help promote the reduction of HgBr_2 to Hg^0 in the downstream SnCl_2 impinger. The decrease in total mercury concentration in Figure 5.5 was calculated using similar conditions; baseline concentration of $25 \mu\text{g}/\text{m}^3$.



Figure 5.4. Losses in total mercury when using different concentrations of the $SnCl_2$ -HCl solution on the total mercury side of the sample conditioning system with 50 ppm bromine (as HBr equivalent), 30 ppm NO, and the high quench temperature profile.

A = $SnCl_2$ as usual (5% $SnCl_2$, 3% HCl)

B = $SnCl_2$ diluted (3% $SnCl_2$, 2% HCl)

C = $SnCl_2$ concentrated (10% $SnCl_2$, 6% HCl)

D = $SnCl_2$ in batch instead of flow mode

E = $SnCl_2$ mixed with 40 ml NaOH (5%)



Figure 5.5. Losses in total mercury when using additional NaOH impingers on the total mercury side of the sample conditioning systems with 50 ppm bromine (as HBr equivalent), 30 ppm NO, and the high quench temperature profile.

A = Conditioning system as usual (SnCl₂ 5% SnCl₂, 3% HCl)

B = NaOH (6M) impinger before the SnCl₂ impinger

C = NaOH (12M) impinger before the SnCl₂ impinger

D = Two NaOH (6M) impingers before the SnCl₂ impinger

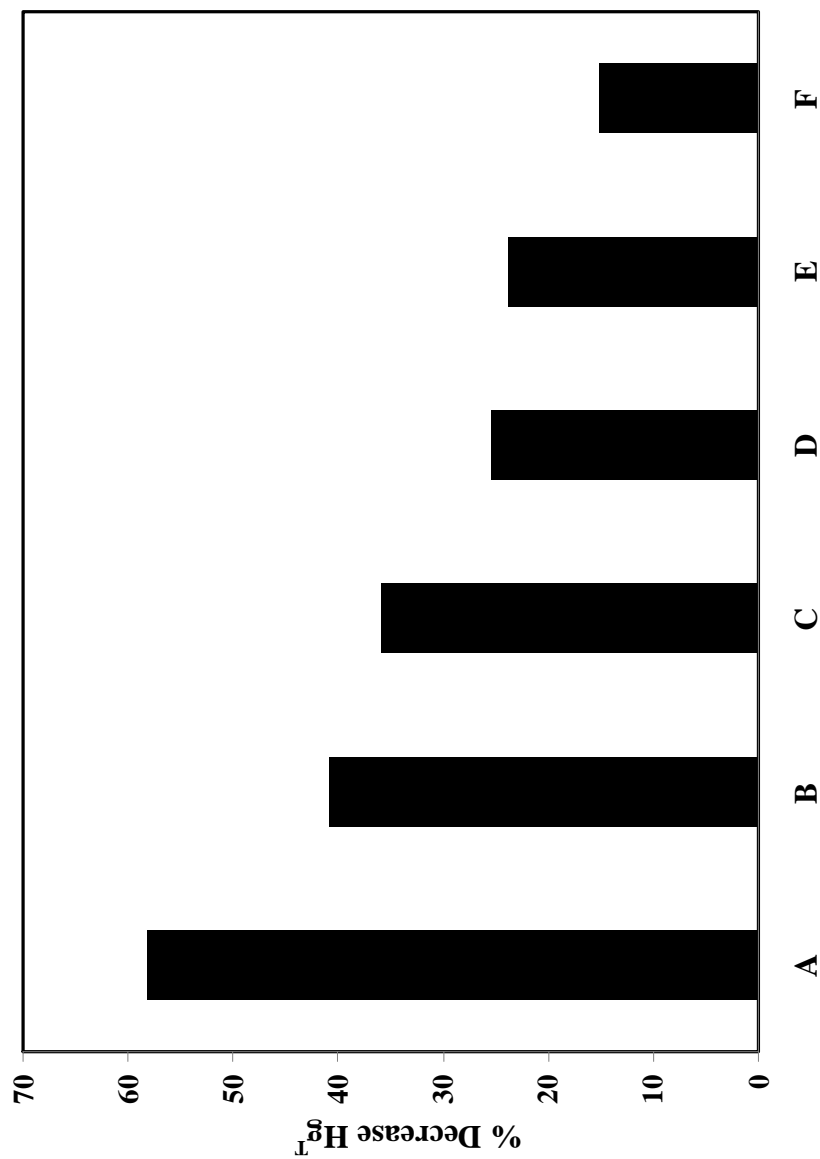


Figure 5.6. Losses in total mercury using a solution of $NH_2OH \cdot HCl$ - $NaOH$ instead of $SnCl_2 \cdot HCl$ on the total mercury side of the sample conditioning system with 50 ppm bromine (as HBr equivalent), 30 ppm NO , and the high quench temperature profile.

A = $SnCl_2$ as usual (5% $SnCl_2$, 3% HCl)
 B = $NH_2OH \cdot HCl$ (30%) impinger before the $SnCl_2$ impinger
 C = $NH_2OH \cdot HCl$ (15%) and $NaOH$ (20%) impinger
 D = $NH_2OH \cdot HCl$ (12%) and then $SnCl_2$ as usual
 E = $NH_2OH \cdot HCl$ (10%) and $NaOH$ (20%) impinger
 F = $NH_2OH \cdot HCl$ (4%) and $NaOH$ (20%) impinger

No SO_2 was added to the reactor and 30 ppm NO and 50 ppm bromine (as HBr equivalent) were present in the system. The percent reduction in the total mercury concentration obtained by the additional NaOH impinger is higher than those shown in Figure 5.4, although this may be due to scatter in the data.

Additional tests were performed in which NaOH was added to the SnCl_2 solution to study the influence of the pH. Although Babi et al. (17) determined that a pH in the range of 3.5-4.5 was enough to get full recoveries of total mercury in the presence of bromine, the laboratory tests performed under the conditions described previously did not show any improvement in mercury recoveries at these pH values.

Figure 5.6 shows the measured decrease in total mercury concentration with 50 ppm bromine (as HBr equivalent), when different mixtures of $\text{NH}_2\text{OH}\cdot\text{HCl}$ and NaOH were used instead of the SnCl_2 -HCl solution. Hydroxyl amine hydrochloride has been used for mercury concentration measurements with urine, blood, and hair samples (19, 20, 21), mostly as a stabilizing agent. It is also a commonly used reducing agent for various applications in synthetic and analytical chemistry.

The decrease in total mercury concentration shown in Figure 5.6 was calculated using the difference between the total side value and the baseline concentration of $25 \mu\text{g}/\text{m}^3$. No SO_2 was added to the reactor and there was 30 ppm NO. The data show that a solution of 4 wt % $\text{NH}_2\text{OH}\cdot\text{HCl}$ and 20 wt % NaOH allowed the measurement of total mercury concentration with a decrease of just 15 %. The stability of the measurements was observed for periods of 3-4 hours and was dependent on the bromine concentration and the frequency of cleaning of the reactor and chiller walls. The longer bromine was in the system the higher the loss of total mercury. This could be an indication of the

accumulation of mercury species on the walls of the reactor, in the impingers, and on the Teflon tubing in the system. Cleaning of the conditioning system prior to bromine injection improved the recovery of total mercury. The presence or absence of a NaOH impinger after the $\text{NH}_2\text{OH}\cdot\text{HCl}$ -NaOH impinger did not make any difference in the measured total mercury concentrations. The results in Figure 5.6 were obtained with a NaOH impinger downstream of the $\text{NH}_2\text{OH}\cdot\text{HCl}$ -NaOH impinger.

Elemental Side of the Conditioning System

The elemental side of the conditioning system showed an unusual behavior in the presence of bromine and SO_2 that suggests that oxidation was occurring either in the KCl impinger or in the downstream NaOH impinger. Figure 5.7 shows that an initial mass balance was closed, with the total and elemental mercury concentrations at similar values as expected. When bromine was added, a decrease in the elemental concentration was observed indicating the extent of mercury oxidation by bromine. When SO_2 was injected, an increase in the elemental mercury concentration was observed. This effect of SO_2 suggests that it is acting as a reducing agent that is removing species that would otherwise oxidize elemental mercury in the impingers. Evidence for liquid-phase reactions is illustrated by Figure 5.8 in which the extent of oxidation in the presence of bromine and SO_2 is similar when the SO_2 is injected through the burner or through the KCl impinger on the elemental side of the conditioning system.

The baseline configuration of the elemental side is a solution of 10 wt % KCl and 0.5 wt % $\text{Na}_2\text{S}_2\text{O}_3$ followed by a 5 wt % NaOH solution as shown in Figure 5.2. To

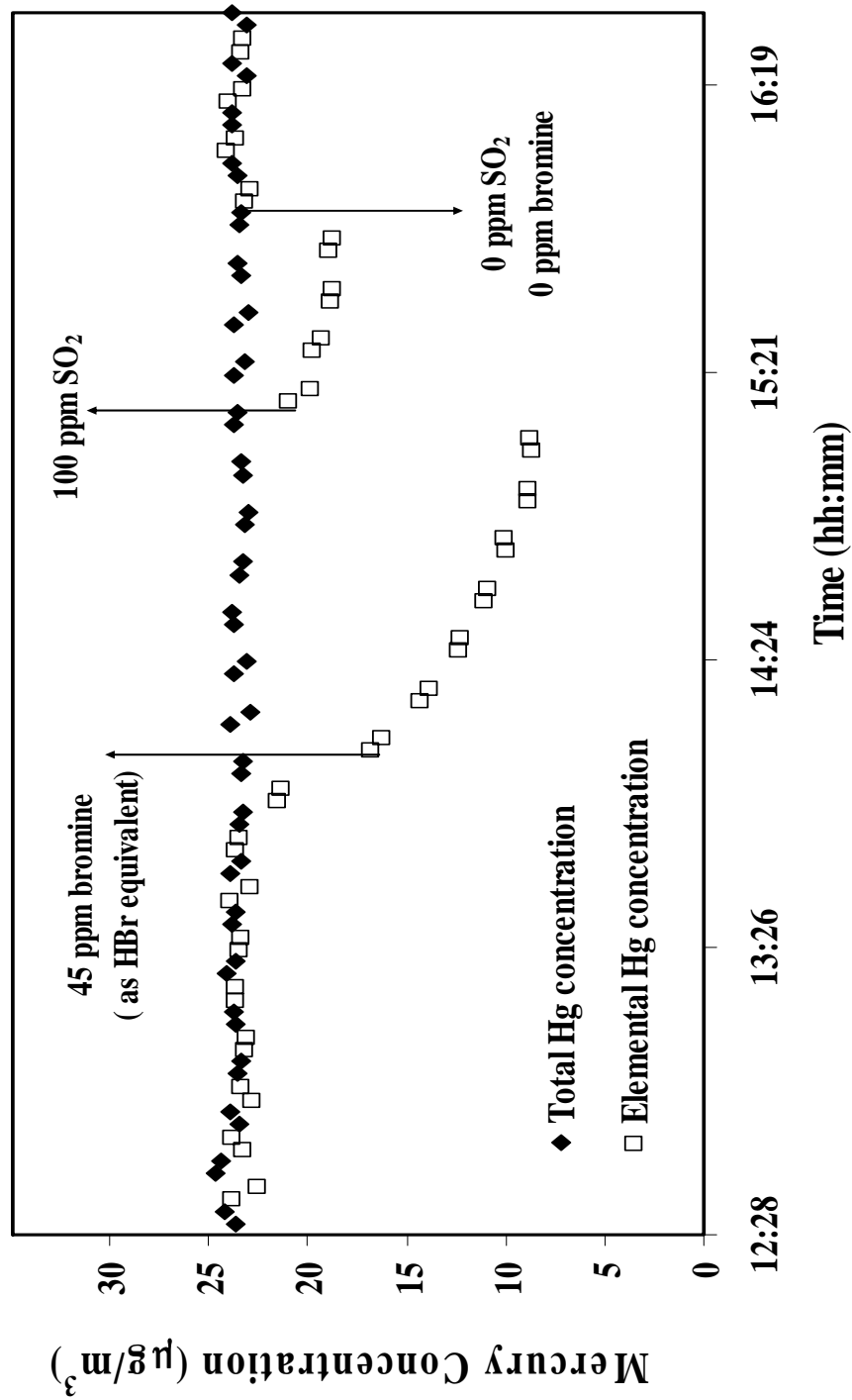


Figure 5.7. Extent of mercury oxidation in presence of 45 ppm bromine (as HBr equivalent) and 100 ppm SO₂. Usual configuration of the elemental side of the conditioning system (see Figure 5.2). Hg^T = Total mercury concentration (elemental plus oxidized mercury, µg/m³). Hg⁰ = Elemental mercury concentration (µg/m³).

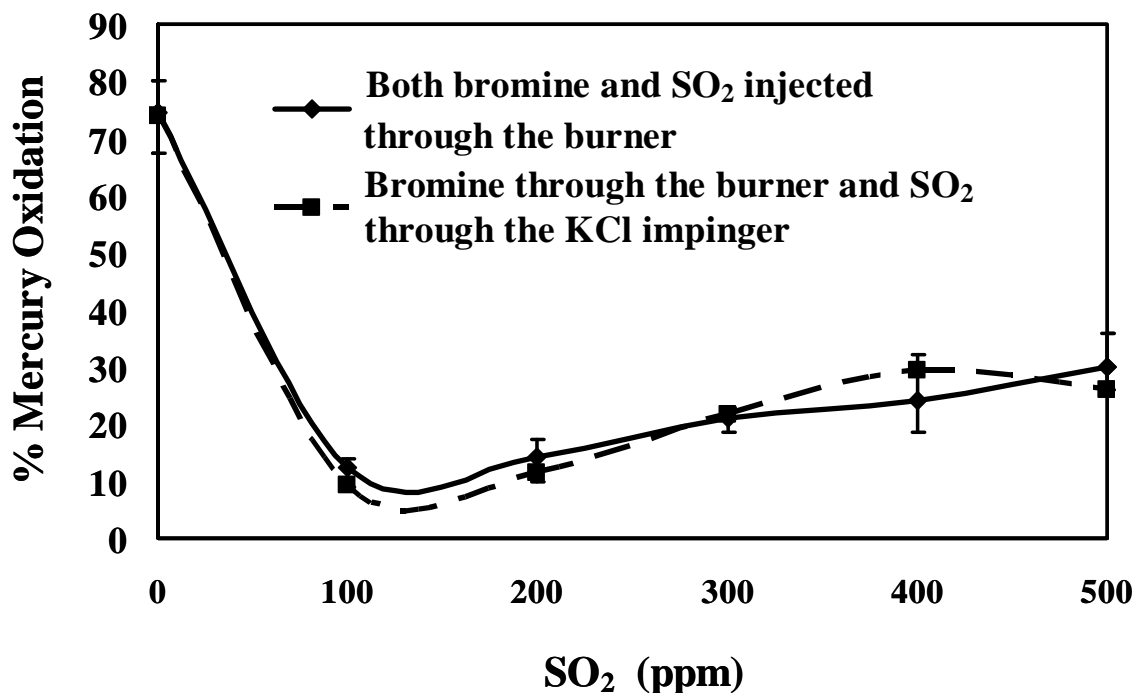


Figure 5.8. Extent of mercury oxidation in the presence of 40 ppm bromine (as HBr equivalent) and SO₂. Usual configuration of the elemental side of the conditioning system (see Figure 5.2). SO₂ injected at two different points along the system, the burner and the KCl impinger.

determine if the composition of these solutions had any impact on the extent of oxidation, the following tests were performed: (1) KCl solution prepared without thiosulfate, (2) KCl solution changed to a THAM/EDTA solution, and (3) a single NaOH impinger on the elemental side of the conditioning system. For these tests the decrease in elemental mercury concentration was measured as a function of the bromine and SO₂ concentration. Figure 5.9 shows that the extent of the decrease in elemental mercury concentration (compared to the baseline value) was similar for all the solutions considered. In presence of 500 ppm SO₂, the extent of the decrease in elemental mercury was also comparable for the four conditions. These results are consistent with the hypothesis that SO₂ is preventing the oxidation of elemental mercury in the elemental side of the conditioning system.

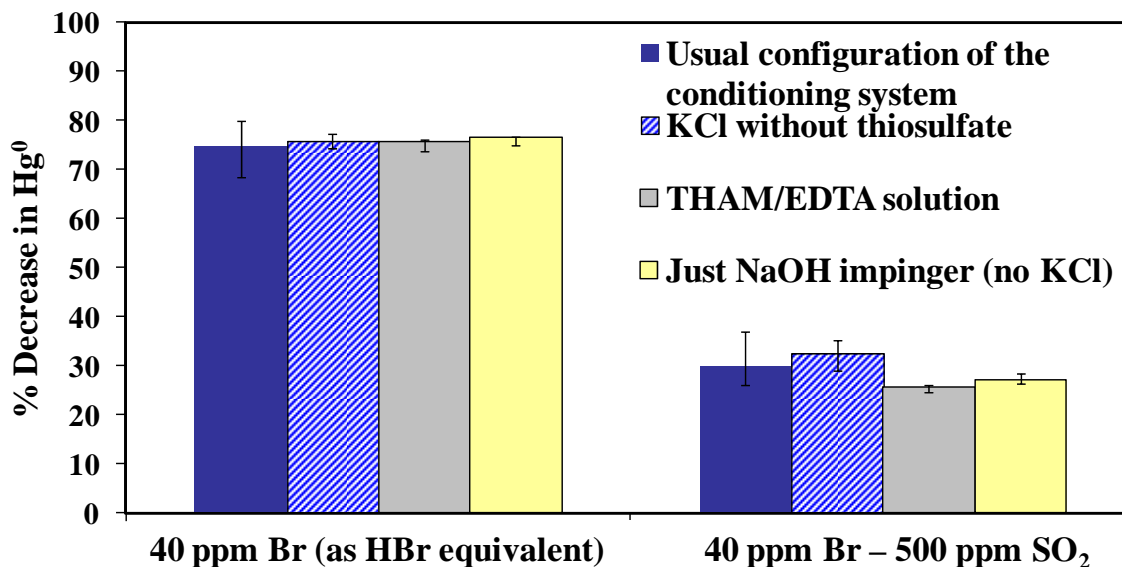


Figure 5.9. Percent of decrease in elemental mercury concentration as a function of the bromine and SO₂ concentrations in the system. Four different configurations of the elemental side of the conditioning system were considered.

To determine the extent of oxidation that is due only to gas phase reactions, additional tests were performed with the objective of removing SO₂ upstream of the KCl impinger. Two configurations were tried: (1) a hydrated lime bed at 150⁰C upstream of the KCl impinger and (2) an additional NaOH impinger upstream of the KCl impinger. Figure 5.10 shows the extent of oxidation obtained with the usual configuration of the conditioning system and these two modifications. The additional NaOH impinger and lime bed did not eliminate the effect of SO₂. This may be due to SO₂ reacting with oxidants in the added NaOH impinger or to by-passing of the lime bed.

Based on the results obtained in this study, the configuration of the wet conditioning system for mercury speciation measurements was modified as shown in Figure 5.11 to avoid the total mercury losses and liquid phase interactions in presence of bromine sulfur dioxide.

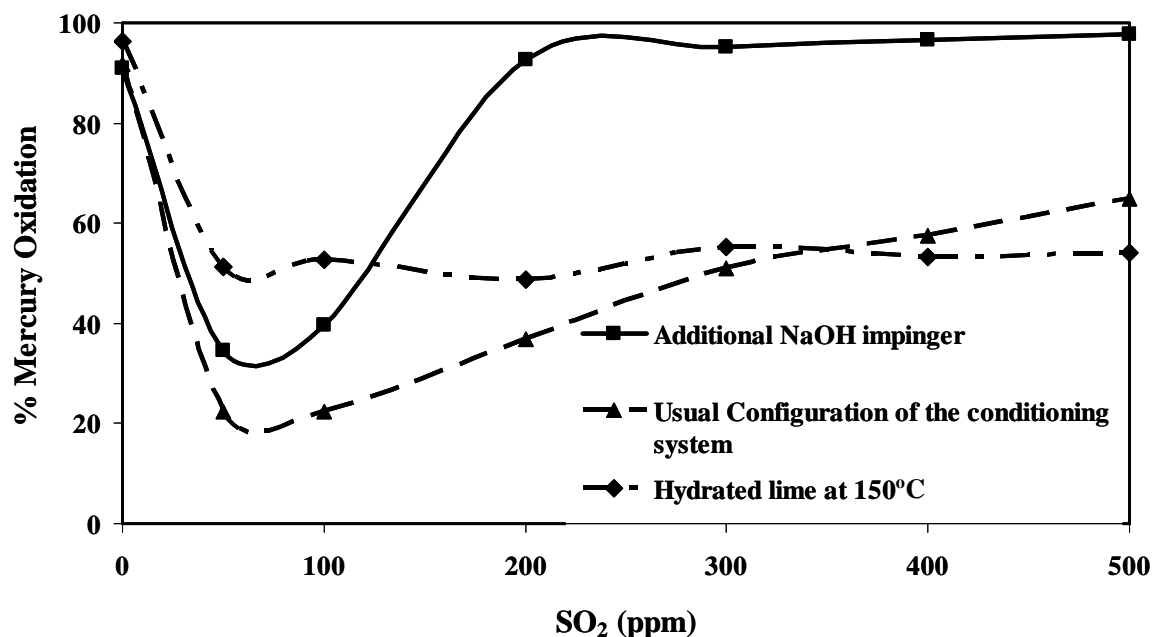


Figure 5.10. Extent of mercury oxidation in presence of 50 ppm bromine (as HBr equivalent) and SO₂. Three different configurations on the elemental side of the conditioning system. The total side of the conditioning system used for these measurements is the one shown in Figure 5.11.

Discussion

Although bromine has become an interesting alternative for increasing the extent of mercury oxidation, reports on its effects on mercury oxidation and measurements are scarce. A few pilot-scale reports cite some bias in total mercury measurements in the presence of bromine when wet conditioning systems are used for mercury speciation. Industrial scale tests by Berry et al. (15) suggest that replacing metallic and glass surfaces by Teflon and quartz, as well as the use of dry based methods help decrease losses in total mercury. Under our experimental conditions there was no contact of the flue gas with metallic surfaces; however, the impingers as well as some components of the chiller

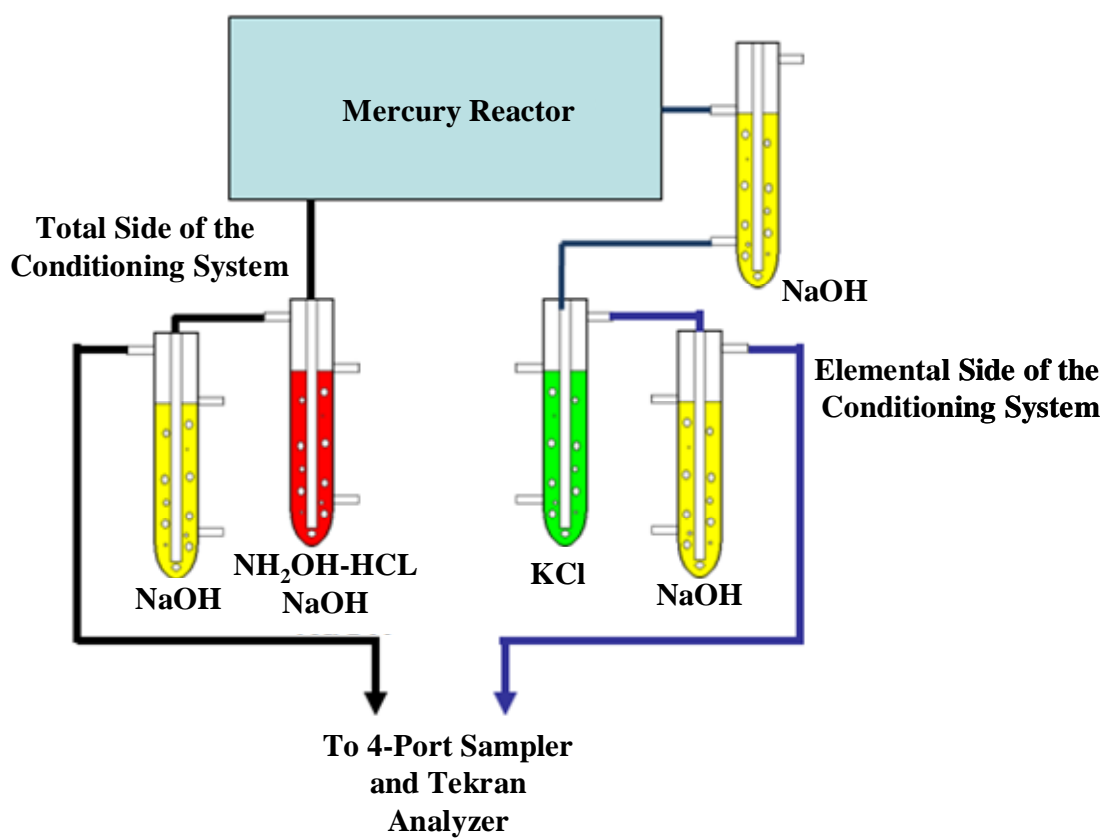


Figure 5.11. Optimal configuration of the conditioning system to measure mercury speciation in presence of bromine and sulfur dioxide.

were made of glass. No significant accumulation of bromine or oxidized mercury species on the impinger walls was detected in this study, based on the fact that cleaning of the impingers did not affect the observed extent of oxidation. In contrast, a frequent cleaning of the chiller was necessary to avoid bias, possibly from glass-flue gas interactions. These interactions were considerably decreased by the new configuration of the conditioning system shown in Figure 5.11. On the total side, the stannous chloride- hydrochloric acid solution was changed to an hydroxyl-amine hydrochloride-sodium hydroxide solution while on the elemental side an additional sodium hydroxide impinger was installed upstream of the potassium chloride impinger to remove sulfur dioxide (see Figure 5.11).

The laboratory scale experiments of Cao et al. (16) also show the importance of cleaning the sampling probe. They studied mercury transformations in the presence of bromine in flue gases generated from the burning of bituminous and Powder River Basin coals. The authors used an inertial sampling probe coupled to an Ontario hydro method and CEM for mercury measurements. They purged and cleaned the sample probe to eliminate apparent losses of mercury in their measurement system.

Babi et al. (17) investigated interferences in continuous flow techniques for mercury measurements in the presence of iodine or bromine. Their work is unique in that they studied oxidation by BrCl. They used a Tekran Series 2600 CVAFS Mercury system configured in accordance with USA EPA Method 1631. This method included a SnCl₂-HCl solution as a reducing agent followed by a NaOH solution. At a mercury concentration of 5 ng/L and 4 % BrCl, the mercury recovery was zero. Babi et al. (17) tested different methods to recover mercury in the presence of bromine and iodine: (1) increasing the reaction time between the sample and the SnCl₂ solution; (2) pH

adjustments of the SnCl_2 solution to destroy possible Hg-Br and Hg-I complexes; (3) increasing the SnCl_2 solution concentration; and (4) replacing the SnCl_2 solution by a potassium borohydride (KBH_4) solution. The authors concluded that pH adjustments to the SnCl_2 solution to 3.5 to 4.5 gave full recovery of mercury in the presence of bromine.

Our results did not show any improvement in mercury recovery at these pH levels and we found that at pH greater than 5, tin hydroxides precipitated. Babi et al. (17) reported that a KBH_4 solution also helped with the measurement of total mercury but he raised questions about its stability. Our tests with KBH_4 as a reducing agent were unsuccessful and gave erratic results.

Regarding the elemental side of the conditioning system, Figures 5.7 and 5.10 show profound effects of SO_2 on the oxidation of mercury by bromine. Parallel experiments conducted with chlorine show no impact of SO_2 (13). A possible reason for this difference is that at equilibrium, below 400°C , Br_2 is the dominant bromine species whereas for chlorine, HCl is dominant. Others (Wang et al. (22)) have noted the possibility of liquid phase oxidation of mercury by bromine or the reduction by species derived from SO_2 of oxidized mercury to elemental (23-27).

The sodium hydroxide impingers on both sides of the wet conditioning system may also be the location of mercury oxidation by bromine. J. Hendrix (29) observed the formation of bromated and hypobromite species when Br_2 was bubbled through aqueous NaOH solutions:



He used reducing agents to prevent the formation of the bromate and hypobromite. The results in Figures 5.7 and 5.10 suggest that SO_2 is acting as a reducing agent that prevents the oxidation of elemental mercury in the sodium hydroxide impingers by reducing bromate and hypobromite.

Thermodynamic and kinetic calculations show that Br_2 is the primary form of bromine at the exit of the reactor (13). Figure 5.5 provides further evidence for the oxidation of mercury in sodium hydroxide solutions; adding NaOH impingers on the total side of the conditioning system, upstream of the $\text{SnCl}_2\text{-HCl}$ impinger, resulted in increased oxidation. These results suggest that a reducing agent, for example, sodium thiosulfate, should be added to the sodium hydroxide impingers on both side of the condition system to prevent confounding effects (8).

Conclusions

The analysis of gas-phase mercury oxidation by bromine was studied using several different configurations of wet conditioning systems. Conditioning systems that determine total mercury concentrations using aqueous tin chloride solutions were improved by substituting it with a solution of hydroxyl-amine hydrochloride and sodium hydroxide (4 wt % $\text{NH}_2\text{OH-HCl}$, 20 wt % NaOH). The determination of elemental mercury in the presence of SO_2 yielded results that suggest that mercury is being oxidized in the sodium hydroxide impingers. The oxidation is believed to be caused by sodium hypobromite and sodium bromate, both of which are formed when Br_2 is bubbled through aqueous sodium hydroxide. Sulfur dioxide reduces the hypobromite and bromate and prevents them from oxidizing elemental mercury. These results suggest that wet conditioning systems tend to overestimate levels of gas-phase oxidation by bromine. The

addition of a reducing agent such as sodium thiosulfate to the hydroxide impingers should eliminate artificially high oxidation levels. The presence of bromine in the system resulted in a decrease in total mercury concentration with respect to the baseline value. This bias in mercury measurements could be due to a low efficiency of the $\text{SnCl}_2\text{-HCl}$ solution to transform all the oxidized mercury back to elemental in presence of bromine, as required by the mercury analyzer. Different configurations on the total side of the conditioning system were tested to reduce this bias. It was determined that the change of the $\text{SnCl}_2\text{-HCl}$ solution by a 4 wt % $\text{NH}_2\text{OH-HCl}$, 20 wt % NaOH solution reduced the bias by 85-90% for periods of 3-4 hours. The extent of the reduction was dependent on bromine concentration and the frequency of cleaning of the system. A thoughtful cleaning of the reactor and chiller before the tests helped to mitigate the bias in measurements. This suggests that some bromine or oxidized mercury species accumulated on the walls of the reactors and chiller during each test.

The elemental mercury measurements were not biased when bromine was present in the system. However, in presence of bromine and SO_2 an increase in elemental mercury concentration was observed. The bias was completely eliminated by the incorporation of an additional NaOH impinger upstream the KCl impinger on the elemental side of the conditioning system when the SO_2 concentration is higher than 200 ppm. At lower SO_2 concentrations, it is believed that still some liquid phase interactions are occurring inside the NaOH impinger.

References

1. www.epa.gov
2. www.osha.gov
3. www.eia.doe.gov
4. Niksa, S., Helble, J., Fujiwara, N. Kinetic Modeling of Homogeneous Mercury Oxidation: The Importance of NO and H₂O in Predicting Oxidation in Coal-Derived Systems *Environ. Sci. Technol.* **2001**, 35 (18), pp 3701–3706.
5. Naruse, I., Yoshie, R., Kameshima, T., Takuwa, T. Gaseous Mercury Oxidation Behavior in Homogeneous Reaction with Chlorine Compounds. *J. Mat. Cycles Waste Manag.* **2010**, 12 (2), 154-160.
6. Xu, M., Qiao, Y., Zheng, C., Li, L., Liu, J. Modeling of Homogeneous Mercury Speciation Using Detailed Chemical Kinetics. *Combust. Flame.* **2003**, 132(1-2), 208-218.
7. Sliger, R., Kramlich, J., Marinov, N. Towards the Development of a Chemical Kinetic Model for the Homogeneous Oxidation of Mercury by Chlorine Species. *Fuel Process. Tech.* **2000**, 65-66, 423-438.
8. Cauch, B., Silcox, G., Lighty, J., Wendt, J., Fry, A. Confounding Effects of Aqueous-Phase Impinger Chemistry on Apparent Oxidation of Mercury in Flue Gas. *Environ. Sci. Technol.*, **2008**, 42(7), 2594-2599.
9. Cao, Y., Wang, Q., Li, J., Cheng, J., Chan, C., Cohron, M., Pan, W. Enhancement of Mercury Capture by the Simultaneous Addition of Hydrogen Bromide (HBr) and Fly Ashes in a Slipstream Facility. *Environ. Sci. Technol.*, **2009**, 43(8), 2812-2817.
10. Wu, C., Cao, Y., Dong, Z., Cheng, C., Li, H., Pan, W. Mercury Speciation and Removal Across Full-scale Wet FGD Systems at Coal-fired Power Plants. *J. Coal Sci. Eng. (China)* **2010**, 16(1), 82-87.
11. Dombrowski, K., McDowell, S., Berry, M., Sibley, A., Chang, R., Vosteen, B. *The Balance-of-Plant Impacts of Calcium Bromide Injection as a Mercury Oxidation Technology in Power Plants*. A&WMA Mega Symposium, August 2008, Baltimore MD (USA).
12. Linak, W., Ryan, J., Ghorishi, B., Wendt, J. Issues Related to Solution Chemistry in Mercury Sampling Impingers. *J. Air Waste Manag. Assoc.* **2001**, 51 (5), 688-698.

13. Cauch, B., Silcox, Geoffrey D., Lighty, J., Wendt, J., Fry, A., Senior, C. Confounding Effects of Aqueous-Phase Impinger Chemistry on Apparent Oxidation of Mercury in Flue Gases. *Environ. Sci. Technol.* **2008**, 42, 2594-2599.
14. Wang, Z., Pehkonen, S. Oxidation of Elemental Mercury by Aqueous Bromine: Atmospheric Implications. *Atmos. Environ.* **2004**, 38, 3675-3688.
15. Berry, M., Dombrowski, K., Richardson, C., Chang, R., Borders, E., Vosteen, B. *Mercury Control Evaluation of Calcium Bromine Injection into a PRB-Fired Furnace with a SCR*. Presented at Air Quality VI, Arlington, VA, September 2007.
16. Cao, Y., Wang, Q., Chen, C., Chen, B., Cohron, M., Tseng, Y., Chiu, C., Chu, P., Pan, W. Investigation of Mercury Transformation by HBr Addition in A Slipstream Facility with Real Flue Gas Atmospheres of Bituminous Coal and Powder River Basin Coal. *Energy & Fuels*, **2007**, 21, 2719- 2730.
17. Babi, D., Schaedlich FH, Schneeberger DR. Correction Techniques for Iodine and Bromine Interferences in Continuous Flow Aqueous Mercury Analysis. *Anal. Bioanal. Chem.* **2002**, 374(6), 1022-1027.
18. Fry, A. Experimental and Kinetic Modeling Investigation of Gas-Phase Mercury Oxidation Reactions with Chlorine. PhD Diss. University of Utah, 2008.
19. Bailey, B., Lo, F. Automated Method for Determination of Mercury. *Anal. Chem.* **1971**, 43 (11) , 1525-1526.
20. Rio-Segade, S., Bendicho, C. Determination of Total and Inorganic Mercury in Biological and Environmental Samples with On-line Oxidation Coupled to Flow Injection-cold Vapor Atomic Absorption Spectrometry. *Spectroch. Acta Part B* **1999**, 54, 1129-1139.
21. Peter, F., Strunc, G. Semiautomated Analysis for Mercury in Whole Blood, Urine and Hair by On-Stream Generation of Cold Vapor. *Clin. Chem.* **1984** 30 (6), 893.895.
22. Wang, Z., Pehkonen, S.O. Oxidation of Elemental Mercury by Aqueous Bromine: Atmospheric Implications. *Atmos. Environ.* **2004**, 38, 3675-3688.
23. Munthe, J.; Xiao, F; Lindqvist, O. The Aqueous Reduction of Divalent Mercury by Sulfite. *Water, Air, Soil Poll.* **1991**, 56, 621-630.
24. Cohen, M. *HYSPLIT Modeling in Phase II of the EMEP Mercury Modeling Intercomparison Study*. Presented at the Expert Meeting on Mercury Model Comparison MSC-East, Moscow, Russia. April 2003.

25. B. Ghorishi, B. Downs, S. Renniger. *Role of Sulfides in the Sequestration of Mercury by Wet Scrubbers*. Presented to: EPRI-DOE-EPA-AWMA Combined Power Plant Air Pollutant Control Mega Symposium. Baltimore, Maryland. August 2006.
26. Pirrone, N.; Mason, R. *Mercury Fate and Transport in the Global Atmosphere Emissions, Measurements and Models*. Springer Science + Business Media, LLC 2009.
27. Chang, J.C.S., Ghorishi, S.B. Simulation and Evaluation of Elemental Mercury Concentration Increase in Flue Gas Across a Wet Scrubber. *Environ. Sci. Technol.* **2003**, 37, 5763-5766.
28. DeBerry, D.W., Blythe, G.M., Pletcher, S., Rhudy, R. *Bench-scale Kinetics Study of Mercury Reductions in FGD Liquors*. Presented at DOE/EPA/EPRI Mega-Symposium, Baltimore, MD, 2006.
29. Hendrix, J. United States Patent 1775598. September 9th 1930.

CHAPTER 6

GAS-PHASE OXIDATION OF MERCURY BY BROMINE AND CHLORINE IN FLUE GAS

Abstract

Bromine has shown a high potential as an elemental mercury oxidant in both industrial and laboratory scale studies. Its impact on the extent of oxidation is dependent on its concentration, temperature of the combustion system and the presence of other halogens and acid gases. This study is focused on determining the effect that the presence of chlorine has on the extent of mercury oxidized homogeneously by bromine. The experimental results showed a slight increase on oxidation by bromine when chlorine was also present in the system; this increase was dependent on chlorine concentration and was more noticeable under low-quench than under high-quench temperature profile conditions. Model predictions followed the same trend of the experimental data but had a tendency to over-predict the extent of oxidation, probably due to the absence of reactions involving BrCl in the kinetic model. For the bromine and chlorine concentrations and temperature profiles considered in this study, model predictions showed that the main oxidized species when both bromine and chlorine are present in the system is HgBr₂. The predicted concentration of BrCl in the system was negligible compared to species such Br₂ and Cl.

Introduction

The combustion of coal is a major source of thermal energy for power generation and process steam. In 2009, 10^9 short tons of coal were consumed in the US; about 44.5 % of it was for electricity generation. Among other pollutants, mercury is emitted as a result of coal burning (1). In 2009, coal consumption for electricity generation released about 40 short tons of mercury to the atmosphere (1). Because of mercury's toxicity and long residence time in the atmosphere, mercury represents a global hazard for the environment and humans (2). Mercury is deposited on land and water in oxidized form. In water, bacteria convert oxidized mercury to methyl mercury which accumulates in cells and is concentrated in the food chain. The consumption of methyl mercury-contaminated fish is the principal route by which people are exposed.

In the flue gas from a typical coal-fired power plant, mercury can be present in elemental and oxidized forms. The oxidized form is water soluble and can generally be collected by existing particulate and SO₂ control devices. Elemental mercury is difficult to capture because it is sparingly soluble in water and is highly volatile at typical air pollution control temperatures. A better understanding of mercury speciation and oxidation mechanisms under typical combustion conditions is essential for the development of mercury control strategies. Techniques that convert elemental mercury to its oxidized forms under postcombustion conditions are desirable.

Few studies on the effect of mixtures of bromine and chlorine on mercury oxidation have been published. The work of Qiu et al. (3) suggests that bromine activates chlorine species, increasing the extent of oxidation beyond that caused by bromine or chlorine alone. Qiu et al. (3) studied the thermodynamics and kinetics of bromine

monochloride (BrCl). They determined that the major oxidized species in the presence of bromine and chlorine was HgCl_2 instead of HgBr_2 . The formation of BrCl was also studied by Cao et al. (4), who suggested that bromine could improve the kinetics of mercury oxidation by promoting the formation of activated chlorine.

In this dissertation, we measure the extents of gas-phase oxidation by chlorine and bromine and investigate the effect of their simultaneous presence. Two temperature profiles and several different halogen concentrations are examined. In addition, several sets of kinetics from the literature were used to predict the extent of oxidation using CHEMKIN 4.1 software. This study presents some of the first laboratory-scale data generated on bromine-mercury reactions and should be useful for validation of kinetics and the development of control strategies for mercury.

Experimental

The reactor used in this study is a 50-mm OD x 47-mm ID quartz tube (132 cm in length) located along the center of a high-temperature Thermcraft heater. The tube extends 79 cm below the heater, is temperature controlled, and has a quartz sampling section at the bottom with a capped end (5). The peak gas temperature in the electrically heated zone was about 1080°C.

A methane-fired, premixed burner made of quartz glass supplied realistic combustion gasses to the reactor. All reactants were introduced through the burner and passed through the flame to create a radical pool representative of combustion systems. The burner heat input was about 300-W, producing 6 slpm of combustion gases. The source of elemental mercury in the reactor was a PS Analytical Mercury Calibration Gas Generator or “CavKit”.

Two quench rates of representative of industrial conditions shown in Figure 6.1, were used in these experiments: 440 K/s (high-quench) and 210 K/s (low-quench). The low temperature region (around 350°C), extends over 3 seconds with the high-quench profile and represents flue-gas temperatures at the end of the convective pass of a boiler. These low temperatures were necessary for mercury oxidation reactions to occur.

For mercury analysis, two sample streams were taken from the bottom of the reaction chamber and introduced into the wet-chemical conditioning system, shown in Figure 6.2. In the baseline conditioning system, one stream was bubbled through a 4 % $\text{NH}_2\text{OH-HCl}$ and 20 % NaOH solution to reduce all mercury to elemental form and through a second impinger containing a 5 % NaOH solution to remove acid gases. This stream was analyzed for the total mercury concentration. The other stream was passed through a set of three impingers, the first one containing a 5 % NaOH solution, the second a 10 wt% KCl and 0.5 wt% $\text{Na}_2\text{S}_2\text{O}_3$ solution to capture oxidized mercury. Sodium thiosulfate was added to prevent oxidation of elemental mercury by halogens in solution (6). Finally, the solution was bubbled through another 5 wt % NaOH solution. This stream represented the elemental mercury concentration present in the system. The impingers had a flow-through arrangement on the liquid side, so that they were continually being refreshed. The two sample streams passed through a chiller to remove any water. A Tekran 2537A mercury analyzer was used to measure the elemental mercury concentration of each stream. A four-port sampler controlled which stream the Tekran Analyzer sampled. The concentration of oxidized mercury was calculated from the difference between the total and elemental mercury concentrations.

The major flue gas components are shown in Table 6.1. The gases and vapors

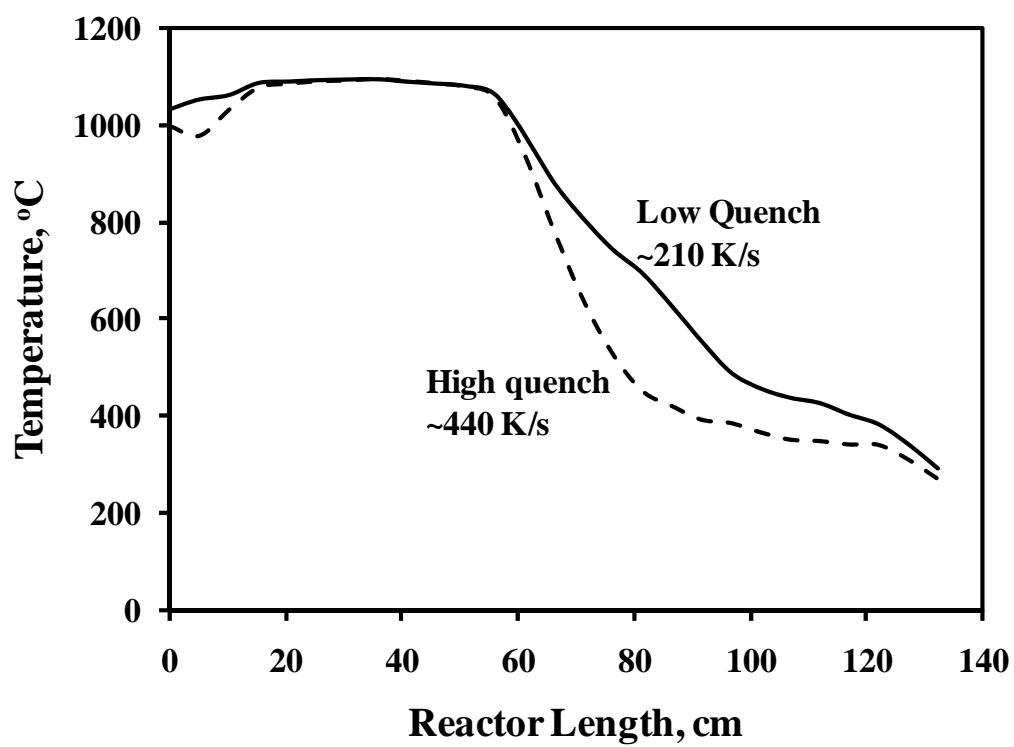


Figure 6.1. Temperature profiles in laboratory furnace.

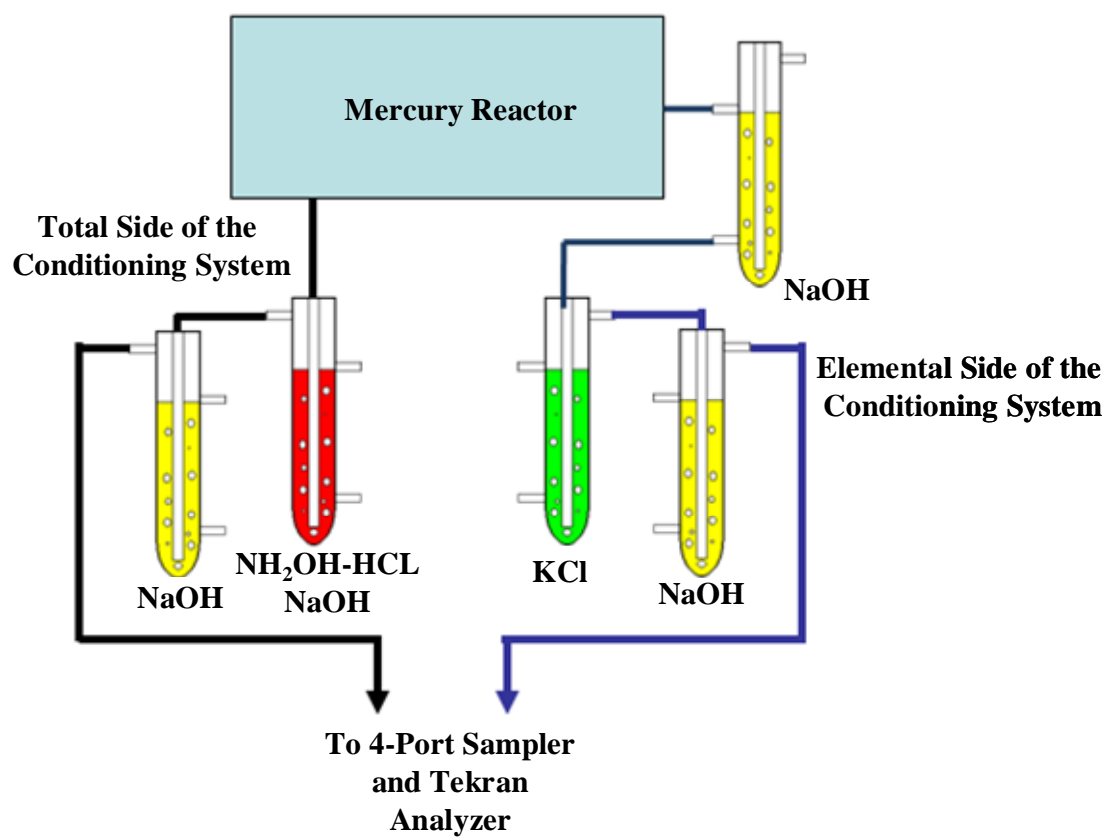


Figure 6.2. Sample conditioning system.

Table 6.1. Flue gas composition for experiments.

Species	Concentration
O₂	0.8 vol. %
H₂O	16.5 vol %
CO₂	7.7 vol. %
NO	30- 500 ppm
SO₂*	0 - 500 ppm
HCL**	0 - 500 ppm
HBr***	0 - 50 ppm
Hg⁰	25 g/Nm ³

* Bottle composition 6000 ppm (SO₂) in air

** Assuming all chlorine added as HCL (bottle composition 6000 ppm Cl₂ in air).

*** Assuming all bromine added as HBr (bottle composition 3000 ppm Br₂ in air).

entering the reactor passed through the methane fired burner and their concentration was measured using California Analytical Instruments Analyzers ZRH Infrared Gas Analyzer for CO and CO₂, Paramagnetic Oxygen Analyzer Model 100P and NOx Analyzer Model 300-CLD.

Kinetic Modeling

CHEMKIN 4.1 was used as the computational platform to simulate homogeneous mercury oxidation using several sets of published and unpublished kinetics.

The kinetic model did not include reactions between mercury and interhalogen species like BrCl. The formation of this species was predicted but at extremely low concentration for the conditions of our experiments. CHEMKIN has modules to describe perfectly stirred reactors (PSR) and plug-flow reactors (PFR). To simulate the methane-

fired burner, a PSR was used. The kinetic mechanism and thermodynamic inputs for this reactor were specified by the GRI mechanism incorporated in the CHEMKIN 4.1 software.

The combustion products leaving the burner were the input for a PFR. The temperature profile and dimensions for the PFR were specified to match the experimental conditions. A schematic of the PSR/PFR system used for the CHEMKIN 4.1 simulations is shown in Figure 6.3. The halogens were added as hydrochloric and hydrobromic acids.

Results and Discussion

Main Reaction Paths for Mercury Oxidation by Chlorine

Several reaction mechanisms were examined and included hydrocarbon chemistry and submodels for Hg, chlorine, bromine, SO_x, and NO_x (7-27). The extent of oxidation by chlorine was most accurately predicted by the mechanism and parameters proposed by Xu et al. (25). Using the high-quench temperature profile and 500 ppm Cl, three of the reactions from this mechanism were found to have a significant impact on the formation of HgCl₂. In the first line of Table 6.2, the predicted level of baseline oxidation, with no reactions removed from the Xu et al. (25) mechanism, is 11.75 %. The level of oxidation rises to 20.52 % if the reaction $\text{HgCl} + \text{HCl} = \text{HgCl}_2 + \text{H}$ is turned off. Oxidation completely ceased if either $\text{Hg} + \text{Cl} + \text{M} = \text{HgCl} + \text{M}$ or $\text{HgCl} + \text{Cl}_2 = \text{HgCl}_2 + \text{Cl}$ were removed. Removing the reaction $\text{HgCl} + \text{HCl} = \text{HgCl}_2 + \text{H}$ promoted oxidation because the reverse reaction consumes HgCl₂. This analysis shows that mercury oxidation by chlorine is a two-step process that is controlled by the reactions $\text{Hg} + \text{Cl} + \text{M} = \text{HgCl} + \text{M}$ and $\text{HgCl} + \text{Cl}_2 = \text{HgCl}_2 + \text{Cl}$, and the formation of HgCl is the rate controlling step.

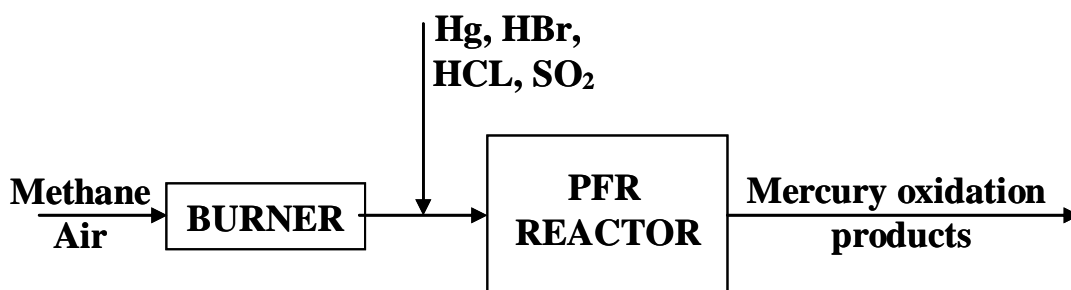


Figure 6.3. Schematic representation of the homogeneous reactor for the CHEMKIN 4.1 model.

Table 6.2. Results of reaction sensitivity analysis on the Xu, Hg-Cl (25) reaction set. Note that the reaction $\text{HgCl}_2 + \text{H} = \text{HgCl} + \text{HCl}$ consumes HgCl_2 . The high-quench rate was used and the concentration of chlorine was 500 ppm as HCl equivalent.

Reaction removed	% Hg Oxidation
None	11.75
$\text{HG} + \text{CL} + \text{M} = \text{HGCL} + \text{M}$	-0.48
$\text{HG} + \text{CL}_2 = \text{HGCL} + \text{CL}$	11.76
$\text{HG} + \text{HOCL} = \text{HGCL} + \text{OH}$	12.27
$\text{HG} + \text{HCL} = \text{HGCL} + \text{H}$	11.75
$\text{HGCL} + \text{CL}_2 = \text{HGCL}_2 + \text{CL}$	-0.33
$\text{HGCL} + \text{HCL} = \text{HGCL}_2 + \text{H}$	20.52
$\text{HGCL} + \text{CL} + \text{M} = \text{HGCL}_2 + \text{M}$	11.68
$\text{HGCL} + \text{HOCL} = \text{HGCL}_2 + \text{OH}$	11.75
$\text{HG} + \text{CLO} = \text{HGO} + \text{CL}$	11.6
$\text{HGO} + \text{HCL} = \text{HGCL} + \text{OH}$	11.72
$\text{HGO} + \text{HOCL} = \text{HGCL} + \text{HO}_2$	11.75
$\text{HG} + \text{CLO}_2 = \text{HGO} + \text{CLO}$	11.75
$\text{HG} + \text{O}_3 = \text{HGO} + \text{O}_2$	11.75
$\text{HG} + \text{N}_2\text{O} = \text{HGO} + \text{N}_2$	11.75

The ROP analysis in Figure 6.4 shows that the reaction $\text{HgCl} + \text{Cl}_2 = \text{HgCl}_2 + \text{Cl}$ contributes more than 90% of the main oxidation product, HgCl_2 . The reaction $\text{Hg} + \text{Cl} + \text{M} = \text{HgCl} + \text{M}$ is the main source of HgCl .

Main Reaction Paths for Mercury Oxidation by Bromine

A similar analysis was performed for mercury oxidation via bromine using a mechanism developed by Bozzelli et al. (28). The results are shown in Table 6.3. One reaction at a time was removed from the mechanism and the resulting oxidation using the HQ temperature profile and 50 ppm Br (as HBr equivalent) was compared to the full mechanism. One reaction accounted for nearly all mercury oxidation: $\text{Hg} + \text{Br}_2 = \text{HgBr}_2$.

The Separate Effects of Bromine and Chlorine

The extent of mercury oxidation was measured at chlorine and bromine concentrations ranging from 0-500 ppm and 0-50 ppm at the high-quench rate. A comparison with model predictions is given in Figure 6.5, parts (a) and (b). Bromine (Figure 6.5b) is seen to be a more effective oxidant than chlorine (Figure 6.5a), as reported in previous studies (29, 30, 31). The higher reactivity of bromine may be due to the predominance of Br_2 rather than HBr at temperatures below 400°C. Hydrochloric acid is the dominant chlorine species at all temperatures relevant to mercury oxidation.

The kinetic calculations summarized in Tables 6.2 and 6.3 show that most of the oxidation by bromine can be attributed to the reaction $\text{Hg} + \text{Br}_2 = \text{HgBr}_2$ while the rate limiting step in the two-step oxidation by chlorine is $\text{Hg} + \text{Cl} = \text{HgCl}$. Figure 6.6 shows predicted mole fractions of Br, HBr, and Br_2 for the low- and high-quench conditions. The low-quench profile results in more Br_2 than the high-quench at temperatures below

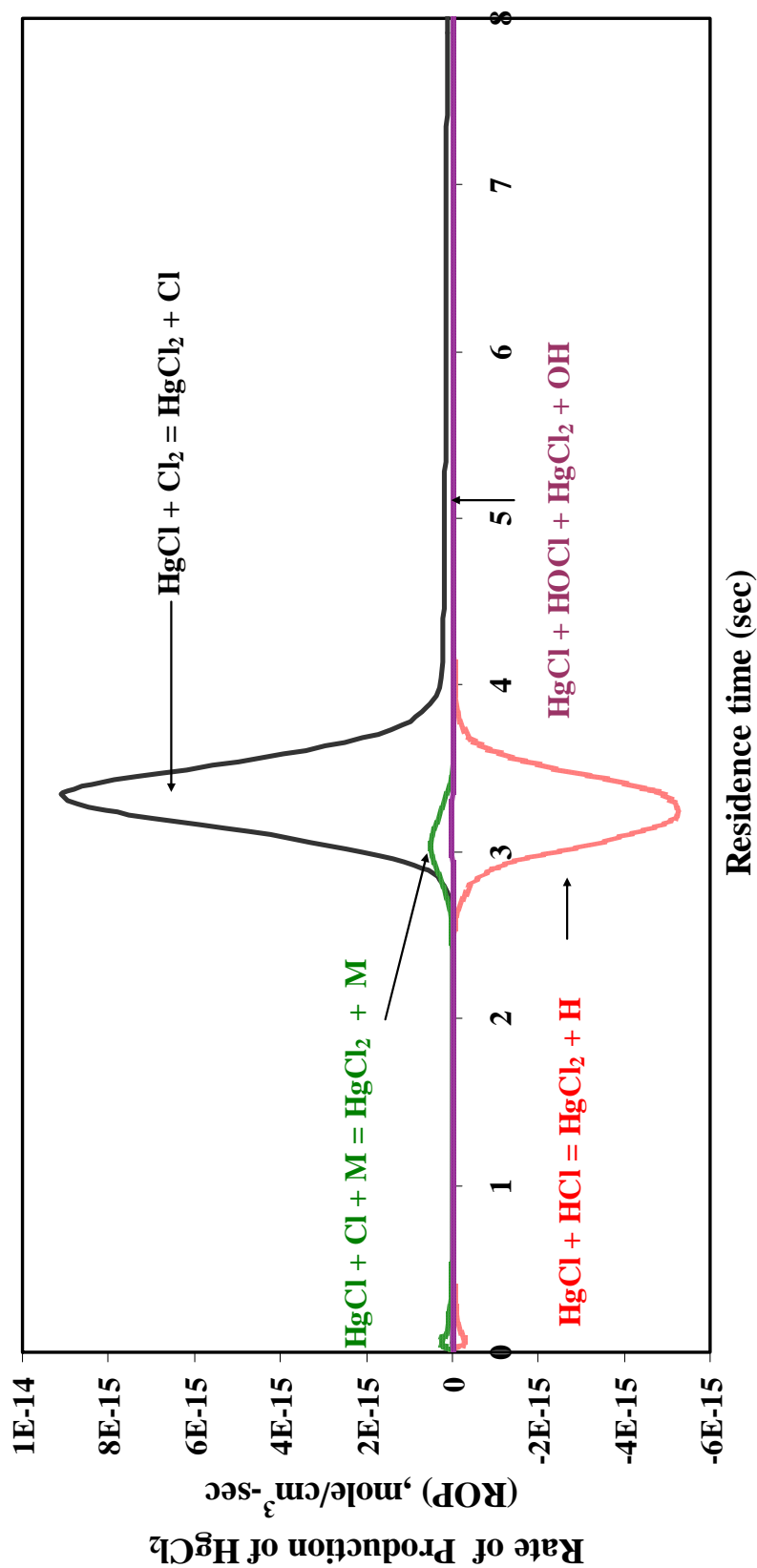


Figure 6.4. Model predictions for the rate of production (ROP) of the reactions involving HgCl_2 . Note that the reaction $\text{HgCl}_2 + \text{H} = \text{HgCl} + \text{HCl}$ consumes HgCl_2 .

Table 6.3. Results of reaction sensitivity analysis with the bromine kinetics of Bozzelli (28) using the high-quench temperature profile and 50 ppm Br (as HBr equivalent).

Reaction removed	% Hg Oxidation
None	95.07
HG + BR <=> HGBR	95.04
HGBR + H <=> HG + HBR	95.07
HGBR + OH <=> HG + BROH	95.07
HGBR + BR₂ <=> HGBR₂ + BR	95.04
HGBR₂ + H <=> HGBR + HBR	95.07
HGBR + BROH <=> HGBR₂ + OH	95.07
HGBR + BRO = HGBR₂ + O	95.07
HGBR + O = BRO + HG	95.07
HG + BR₂ = HGBR₂	-0.01
HGBR + BR <=> HGBR₂	95.06
HG + BR₂ = HGBR + BR	95.07
HGOH + BR <=> HGBROH	95.07
HGOH + BR <=> HGBR + OH	95.07
HGBR + OH <=> HGBROH	95.07
HGO + BR <=> HGBRO	95.07
HGBROH + OH = HGBRO + H₂O	95.07
HGBRO + HO₂ = HGBROH + O₂	95.07

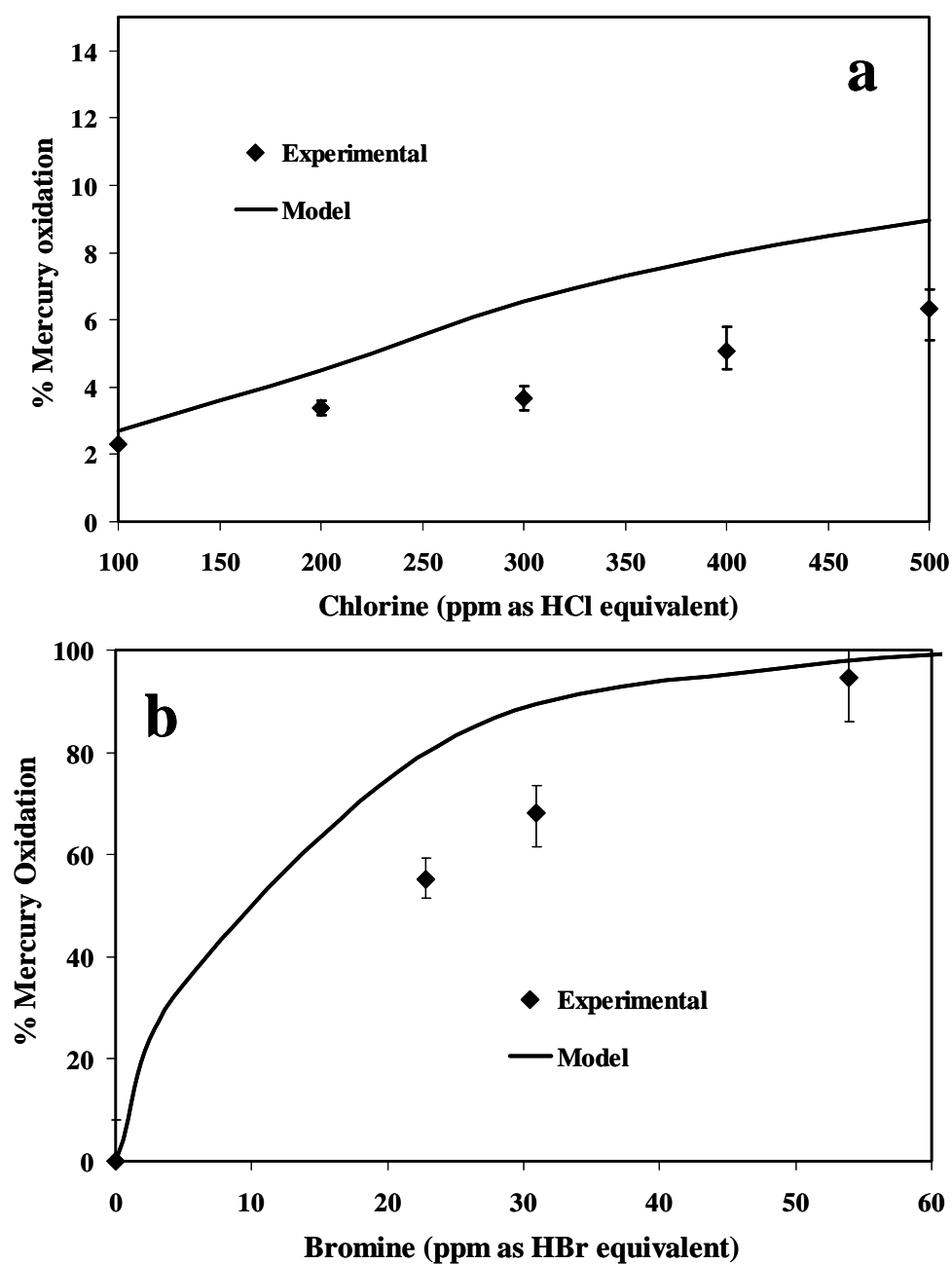


Figure 6.5. Effect of chlorine and bromine on mercury oxidation for the high-quench temperature profile. (a) Effect of chlorine (as HCl equivalent) on mercury oxidation. (b) Effect of bromine (as HBr equivalent) on mercury oxidation.

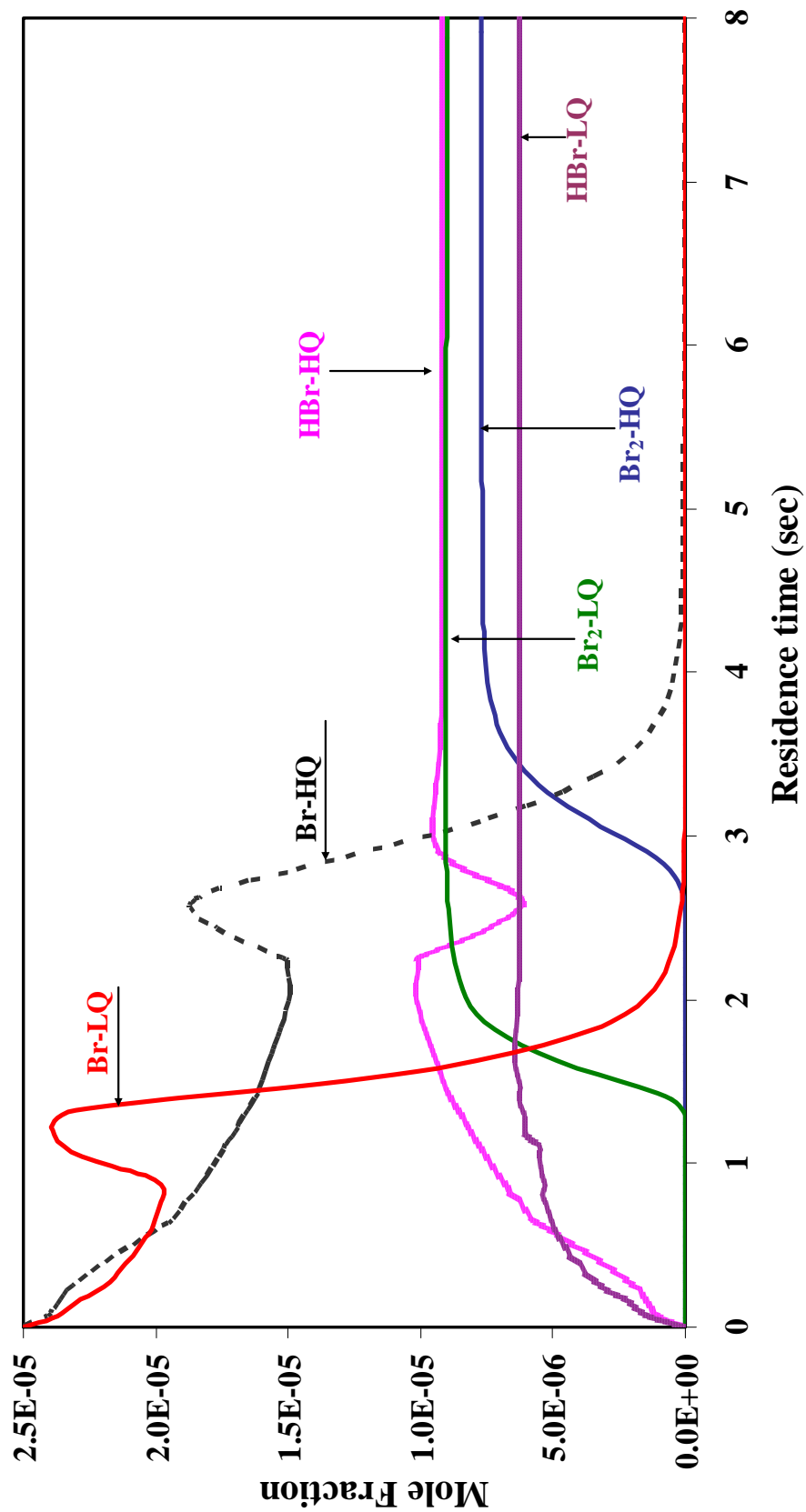


Figure 6.6 Model predictions of the mole fractions of HBr, Br and Br₂ for the high- and low-quench temperature profiles (HQ and LQ).

400°C and this is consistent with the higher levels of oxidation observed experimentally.

Effects of Mixtures of Bromine-Chlorine on Mercury Oxidation

The experimental and modeling results for mercury oxidation by mixtures of bromine and chlorine are presented in this section. To predict the extent of oxidation by bromine and chlorine, mercury-chlorine reaction kinetics from Xu et al. (25), mercury-bromine and chlorine-bromine, kinetics from Bozzelli et al. (28) were included. The expanded kinetic set predicts that with bromine at concentrations between 25 and 50 ppm and chlorine concentrations in the range from 100 to 400 ppm, the major oxidized mercury species is HgBr_2 .

As shown in Figure 6.7, for a bromine concentration of 25 ppm (as HBr equivalent), and the high and low-quench rate, the measured extent of oxidation increased slightly with increasing chlorine concentration at the low-quench condition. The effect of quench rate is pronounced with the low rate resulting in about 80% oxidation and the high rate, 50%. The model overpredicts the extents of oxidation and underpredicts the effects of quench rate.

The data in Figure 6.8 were obtained with the high-quench profile at 25 and 50 ppm bromine. The low-quench profile increased the sensitivity to chlorine, as shown in Figure 6.7, and resulted in higher levels of oxidation. With the high-quench condition there was little impact of chlorine on oxidation. The model overpredicts the extents of oxidation to such an extent that the effects of increasing the bromine concentration are obscured. Figures 6.7 and 6.8 also include predicted levels of oxidation. The model overpredicted oxidation at all conditions but did show the correct trend of increasing oxidation with decreasing quench rate. At all conditions examined, the predicted

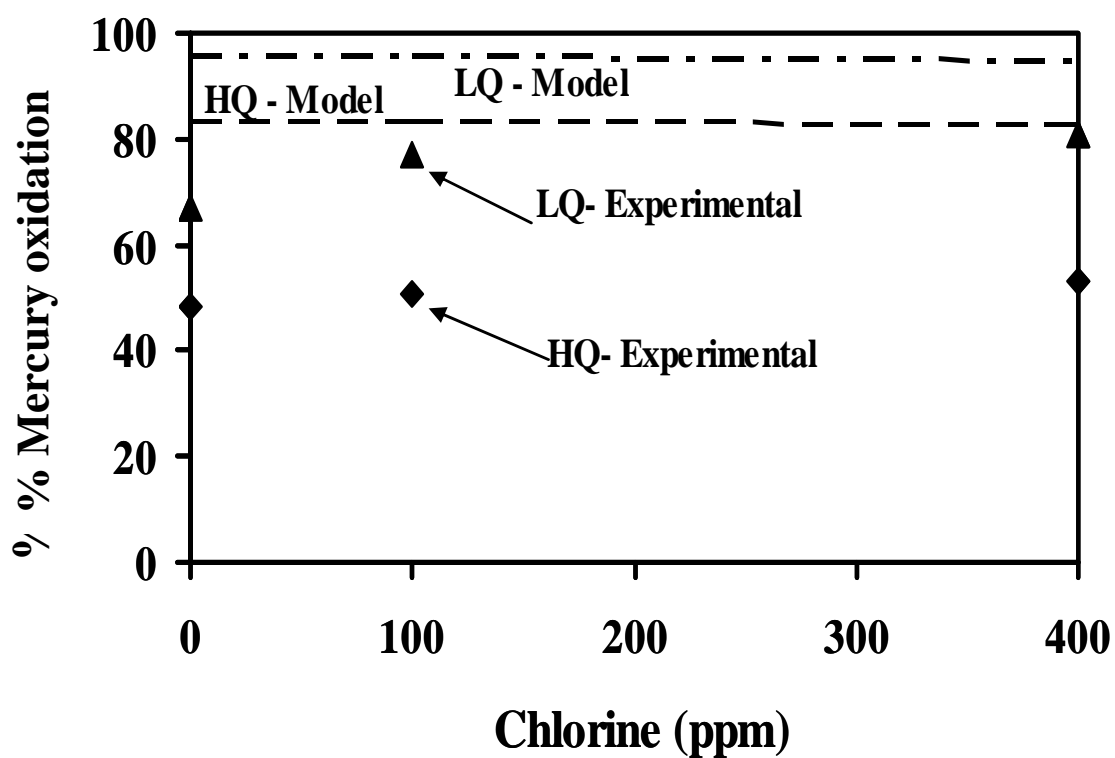


Figure 6.7. Experimental results and model predictions for oxidation by mixtures of bromine and chlorine at the high- and low-quench profiles. Concentrations of chlorine and bromine are ppm as HCl and HBr equivalents. The bromine concentration is constant at 25 ppm.

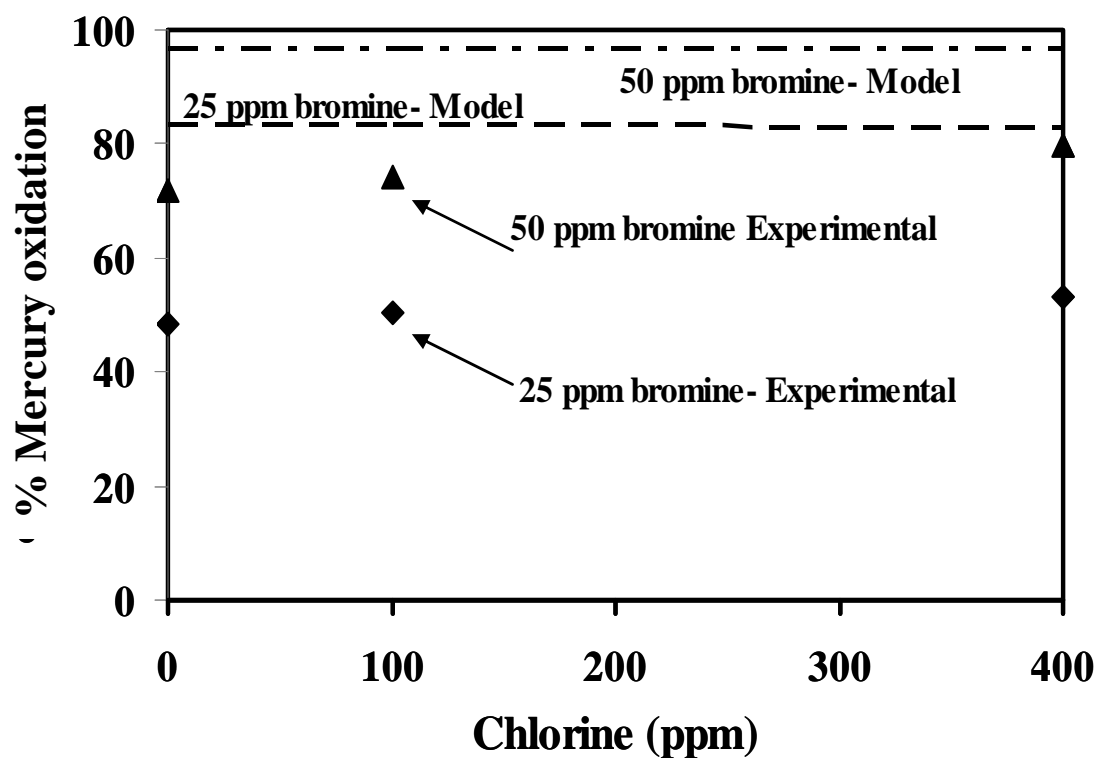


Figure 6.8. Experimental results and model predictions for oxidation by mixtures of bromine and chlorine at the high-quench rate. Concentrations of chlorine and bromine are ppm as HCl and HBr equivalents.

oxidation was insensitive to the concentration of chlorine. This insensitivity could be due to the lack of Hg-BrCl reactions in the kinetic mechanism. Studies performed by Cao et al. (4) under similar experimental conditions, particularly for temperatures lower than 300°C, show that BrCl can be present and they believe it can react with mercury (4).

The experiments performed do not eliminate the possibility of oxidation due to liquid-phase reactions in the sample conditioning system (32-36). Additional tests in which sodium thiosulfate is added to the sodium hydroxide impingers are needed to examine this possibility.

The results shown in Figures 6.7 and 6.8 do not show significant effects of the simultaneous presence of bromine and chlorine on mercury oxidation; however, the kinetic calculations performed by Cao et al. (4) show that under their experimental conditions, the presence of bromine resulted in a considerable increase in oxidation due mostly to the activation of the chlorine species. Their calculations are based on a kinetic mechanism in which the formation of the interhalogen species BrCl results in both the regeneration of molecular chlorine and bromine, and the formation of oxidized mercury species.

A similar theory was presented by Qu et al. (37) who studied the thermodynamics and kinetics of the reaction between bromine and chlorine to form BrCl when 10 ppm Br₂ and 10 ppm Cl₂ were present in the system. They determined that the major oxidized species in the flue gas in the presence of both bromine and chlorine was HgCl₂ instead of HgBr₂. In contrast, our model predictions suggest that for the bromine and chlorine concentrations used in our study at the high- and low-quench temperature profiles, the major oxidized species was HgBr₂. The discrepancy in the observations from the two

studies could be associated with the difference in experimental conditions, halogen concentrations and the molecular form of the halogens injected into the system. In Qu et al. (37), the halogens were combined in their molecular form while in our study they were injected as HCl and HBr and passed through a flame which is expected to have a significant impact on the reaction pathways. This could be a potential reason for the difference in the extent of mercury oxidation reported by Qu et al. (37). They observed extents of oxidation of 100 % and 90 % when 10 ppm Cl_2 and 10 ppm Br_2 were injected into the system, respectively. In contrast, our results showed mercury oxidation on the order of 15 % for concentrations of chlorine (as HCl equivalent) as high as 500 ppm. Additionally, the discrepancies can be associated to the difference in the mercury measuring systems. While we used a wet conditioning system coupled to a Tekran, Qu et al. (37) used UV-vis spectroscopy to measure mercury species.

Studies performed under atmospheric conditions (38-40) show that more mercury is oxidized by either Br_2 or BrCl than by chlorine. Although these results are similar to our experimental findings when both halogens are present, our observations about the formation and effect of BrCl oxidation are different.

At the conditions of our study, both experiments and model predictions showed a small increase in oxidation by bromine with increasing chlorine concentration. To determine if this increase could be explained by the formation of BrCl , an analysis of the rates of production for the main bromine and chlorine species, including BrCl , was performed. The results are summarized in Figure 6.9. Figure 6.9 shows that the predicted BrCl mole fraction is 10^5 times smaller than Br_2 and 10^3 times smaller than Cl_2 . The halogen concentrations in Figure 6.9 were obtained with 50 ppm bromine (as HBr

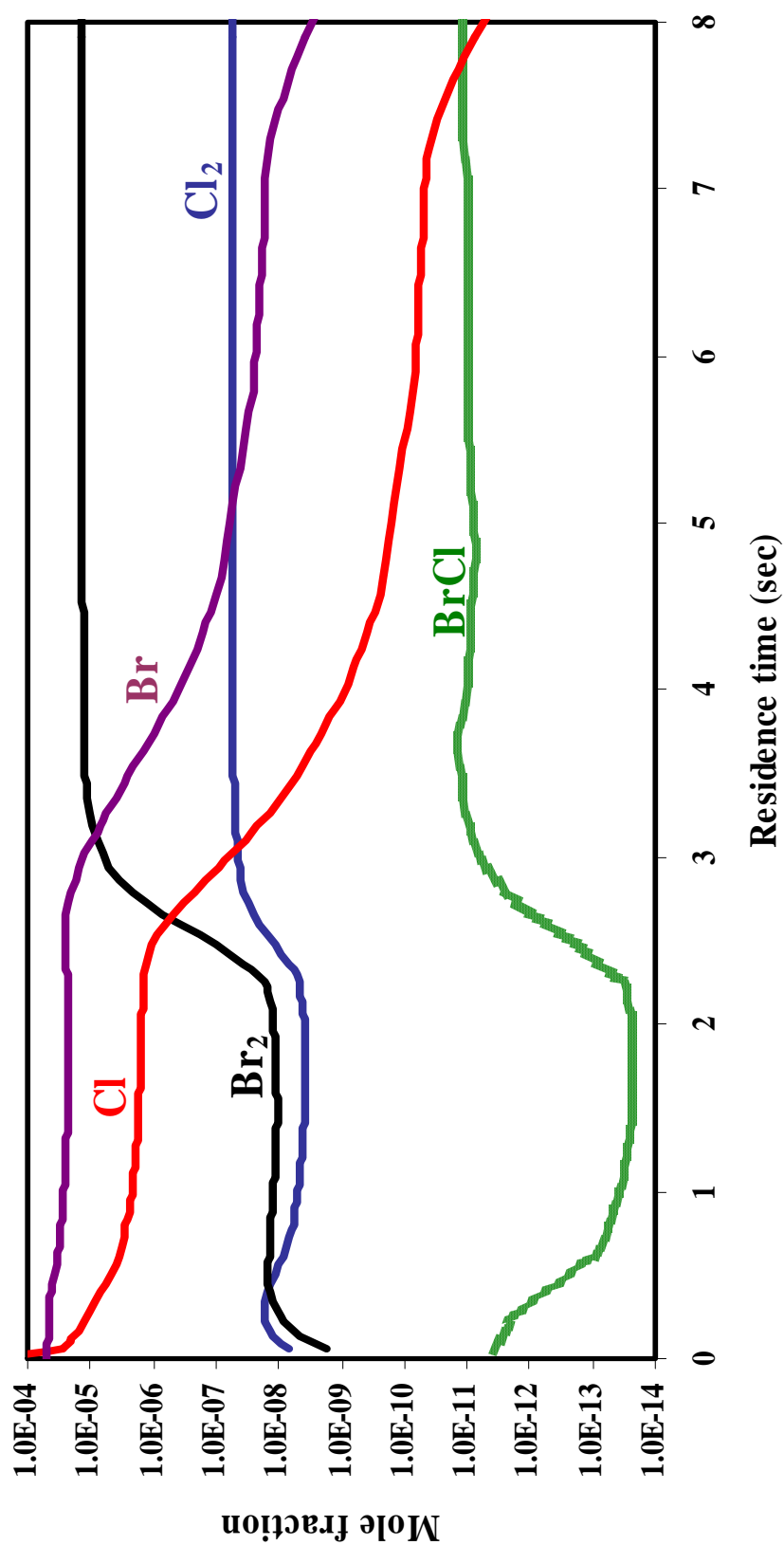


Figure 6.9. Model predictions of the mole fractions of Cl_2 , Br_2 , Br , Cl and BrCl in flue gas with 50 ppm bromine (as HBr equivalent), 400 ppm chlorine (as HCl equivalent), and the high-quench temperature profile.

equivalent), 400 ppm chlorine (as HCl equivalent), and the high-quench temperature profile. The fraction of BrCl is also lower than that predicted for Br and Cl which suggests it would have a minor impact on oxidation.

Note that our kinetics did not account for direct reactions between BrCl and Hg. Our calculations show that with mixtures of bromine and chlorine, the main oxidized species is HgBr₂. Ninety-three % of the total HgBr₂ was derived from the reaction $\text{Hg} + \text{Br}_2 = \text{HgBr}_2$ at bromine and chlorine concentration of 50 and 400 ppm (as HBr or HCl equivalents).

At the conditions examined here, mercury oxidation by mixtures of bromine and chlorine is mostly due to Br₂, and to a lesser extent, Cl. oxidation by BrCl is expected to be negligible and was not accounted for in the predictions.

Conclusions

Five Hg-Cl and three Hg-Br mechanisms, some published and others under development, were evaluated and compared to the gas-phase mercury oxidation data obtained in this study. The calculations confirm that mercury oxidation by chlorine is a two-step mechanism involving the reactions: $\text{Hg} + \text{Cl} + \text{M} = \text{HgCl} + \text{M}$ and $\text{HgCl} + \text{Cl}_2 = \text{HgCl}_2 + \text{Cl}$. The rate controlling step is the formation of HgCl. In the case of oxidation by bromine, a single reaction was responsible for most of the observed oxidation: $\text{Hg} + \text{Br}_2 = \text{HgBr}_2$.

Model predictions showed that concentrations of BrCl are negligible compared to Br, Br₂, Cl and Cl₂. It is expected that mercury oxidation by BrCl is negligible as well.

Measured extents of oxidation showed that the presence of bromine and chlorine caused a limited increase in oxidation compared to what would have been obtained with

bromine alone. This increase was fairly minor and was proportional to the chlorine concentration. The increase was higher at the lower bromine concentration (25 ppm as HBr equivalent) and with the low-quench temperature profile.

The effect of quench rate on oxidation by 25 ppm bromine (as HBr equivalent) was significant with 80% oxidation at low-quench (210 K/s) and 50% at high-quench (440 K/s). Calculations show that this is due to the preferential formation of Br_2 rather than HBr at the low-quench condition.

References

1. www.eia.doe.gov
2. www.epa.gov
3. Qiu, J.; Sterling, R.; Helble, J. *Development of an Improved Model for Determining the Effects of SO₂ on Homogeneous Mercury Oxidation*. Proceedings of the 28th International Technical Conference on Coal Utilization & Fuel Systems, Clearwater, FL, March, 2003.
4. Cao, Y., Gao, Z., Zhu, J. Wang, Q., Huang, Y., Chiu, C., Parker, B., Chu, P., Pan, W. Impacts of Halogen Additions on Mercury Oxidation, in A Slipstream Selective Catalyst Reduction (SCR), Reactor when Burning Sub-Bituminous Coal. *Environ. Sci. Technol.* **2008**, 42, 256–261.
5. Fry, A.; Cauch, B.; Silcox, G.; Lighty, J.; Senior, C. *Experimental Evaluation of the Effects of Quench Rate and Quartz Surface Area on Homogeneous Mercury Oxidation*. in: 31st International Symposium on Combustion, Heidelberg, Germany, August, 2006.
6. Cauch, B., Silcox, Geoffrey D., Lighty, J., Wendt, J., Fry, A., Senior, C. Confounding Effects of Aqueous-Phase Impinger Chemistry on Apparent Oxidation of Mercury in Flue Gases. *Environ. Sci. Technol.* **2008**, 42, 2594-2599.
7. Hall, B.; Schager, P.; Lindquist, O. Chemical Reactions of Mercury in Combustion Flue Gases. *Water, Air, Soil Poll.* **1991**, 56, 3-14.
8. Widmer, N.; Cole, J.; Seeker, W.; Gaspar, J. A. Practical Limitation of Mercury Speciation in Simulated Municipal Waste Incinerator Flue Gas. *Combust. Sci. and Tech.* **1998**, 134, 315-326.
9. Widmer, N.; West, J.; Cole, J. A. *Thermochemical Study of Mercury Oxidation in Utility Boiler Flue Gases*. Proceedings A&WMA Annual Conference, Salt Lake City, UT, June, 2000.
10. Ghorishi, S. Fundamentals of Mercury Speciation and Control in Coal-fired Boilers. in: EPA-600/R-98-014, February 1998.
11. Laudal, D.; Brown, T.; Nott, B. Effects of Flue Gas Constituents on Mercury Speciation. *Fuel Process. Technol.* **2000**, 65-66, 157-165.
12. Sliger, R.; Kramlich, J.; Marinov, N. Towards the Development of a Chemical Kinetic Model for the Homogeneous Oxidation of Mercury by Chlorine Species. *Fuel Process. Technol.* **2000**, 65-66, 423-438.

13. Mamani-Paco, R.; Helble, J. *Bench-scale Examination of Mercury Oxidation Under Non-isothermal Conditions*. Proceedings A&WMA Annual Conference, Salt Lake City, UT, June, 2000.
14. Niksa, S.; Helble, J.; Fujiwara, N. Kinetic Modeling of Homogeneous Mercury Oxidation: the Importance of NO and H₂O in Predicting Oxidation in Coal-derived Systems. *Environ. Sci. Technol.* **2001**, 35 (18), 3701-3706.
15. Niksa, S.; Helble, J.; Fujiwara, N. *Interpreting Laboratory Test Data on Homogeneous Mercury Oxidation in Coal-derived Exhausts*. Proceedings of the 94th Annual Air & Waste Management Association Conference, Orlando, FL, June 2001.
16. Roesler, J.; Yetter, R.; Dryer, F. Detailed Kinetic Modeling of Moist CO Oxidation Inhibited by Trace Quantities of HCl. *Combust. Sci. and Tech.* **1992**, 85, 1-22.
17. Roesler, J.; Yetter, R.; Dryer, F. Kinetic Interactions of CO, NO_x, and HCl Emissions in Post combustion Gases. *Combust. Flame.* **1995**, 100, 495-504.
18. Senior, C.; Lignell, D.; Chen, Z.; Shiley, B.; Sarofim, A. *Modeling Gaseous Mercury Behavior in Practical Combustion Systems*. Proceedings of the International Conference on Air Quality IV, Arlington, VA, September, 2003.
19. Sable, S.; Jong, W.; Spliethoff, H. Combined Homo- and Heterogeneous Model for Mercury Speciation in Pulverized Fuel Combustion Flue Gases. *Energy & Fuels.* **2008**, 22 (1), 321-330.
20. Wilcox, J.; Marsden, D.; Blowers, P. Evaluation of Basis Sets and Theoretical Methods for Estimating Rate Constants of Mercury Oxidation Reactions Involving Chlorine. *Fuel Processing Technology.* **2004**, 85 (5), 391-400.
21. Wilcox, J.; Robles, J.; Marsden, D.; Blowers, P. Theoretically Predicted Rate Constants for Mercury Oxidation by Hydrogen Chloride in Coal Combustion Flue Gases. *Environ. Sci. Technol.* **2003**, 37 (18), 4199-4204.
22. Krishnakumar, B.; Helble, J. Understanding Mercury Transformations in Coal-Fired Power Plants: Evaluation of Homogeneous Hg Oxidation Mechanisms. *Environ. Sci. Technol.* **2007**, 41 (22), 7870-7875.
23. Edwards, J.; Srivastava, R.; Kilgroe, J. A Study of Gas-phase Mercury Speciation Using Detailed Chemical Kinetics. *J. Air & Waste Manage. Assoc.* **2001**, 51, 869-877.
24. Senkan, S. *Survey of Rate Coefficients in the C-H-Cl-O System*. In *Gas-Phase Combustion Chemistry*. Springer-Verlag: New York, 2000; 389-487.

25. Xu, M.; Qiao, Y.; Zheng, C.; Li, L.; Liu, J. Modeling of Homogeneous Mercury Speciation Using Detailed Chemical Kinetics. *Combust. Flame*. **2003**, 132, 208-218.
26. Niksa, S.; Padak, B.; Krishnakumar, B.; Naik, C., Process Chemistry of Br Addition to Utility Flue Gas for Hg Emissions Control. *Energy and Fuels*. **2010**, 24 (2), 1020-1029.
27. N.I.S.T., <http://kinetics.nist.gov/kinetics/index.jsp> 2006.
28. Bozzelli, J. New Jersey Institute of Technology, Personal Communication, 2009-2010.
29. Liu, S., Yan, N., Liu, Z., Qu, Z., Wang, H., Chang, S., Miller, C. Using Bromine Gas to Enhance Mercury Removal from Flue Gas of Coal-Fired Power Plants. *Environ. Sci. Technol.* **2007**, 41, 1405-1412.
30. <http://ieeexplore.ieee.org/stamp/stamp.jsp?arnumber=04535378>.
31. Xie, Z., Sander, R., Poschl, U., Slemr, F. Simulation of Atmospheric Mercury Depletion Events (AMDEs) During Polar Springtime Using the MECCA Box Model. *Atmos. Chem. Phys.* **2008**, 7165-7180.
32. Hedgecock, I., Trunfio, G., Pirrone, N., Sprovieri, F. Mercury Chemistry in the MBL: Mediterranean Case and Sensitivity Studies Using the AMCOTS (Atmospheric Mercury Chemistry Over the Sea) Model. *Atmos. Environ.* **2005**, 39, 7217-7230.
33. Wang, Z., Pehkonen, S. Oxidation of Elemental Mercury by Aqueous Bromine: Atmospheric Implications. *Atmos. Environ.* **2004**, 38, 3675-3688.
34. Laurier, F., Mason, R., Whalin, L., Kato, S. Reactive Gaseous Mercury Formation in the North Pacific Ocean's Marine Boundary Layer: A Potential Role of Halogen Chemistry. *J. Geo. Res.* **2003**, 108, 4529- 4541.
35. Platt, U., Honninger, G. The Role of Halogen Species in the Troposphere. *Chemosphere*, **2003**, 52(2), 325-338.
36. Glasow, R., Kuhlmann, R., Lawrence, M., Platt, U., Crutzen, P. Impact of Reactive Bromine Chemistry in the Troposphere. *Atmos. Chem. Phys.* **2004**, 4, 2481- 2497.
37. Qu, Z., Yan, N., Liu, P., Chi, Y., Jia, J. Bromine Chloride as an Oxidant to Improve Elemental Mercury Removal from Coal-Fired Flue Gas. *Environ. Sci. Technol.* **2009**, 43, 8610–8615.

38. Olbregts, J. Reaction of Chlorine with Bromine. *Inter. J. Chem. Kin.* **1974**, 6, 395-400.
39. Coker, D.F., Watts, R.O. Chemical Equilibria in Mixtures of Bromine and Chlorine. *Mol. Phys.* **1981**, 44(6), 1303-1318.
40. Tellinghuisen, J. Precise Equilibrium Constants from Spectrophotometric Data : BrCl in Br₂/Cl₂ Gas Mixtures. *J. Phys. Chem. A.* **2003**, 107, 753-757.

CHAPTER 7

**THE EFFECTS OF OXY-FIRING CONDITIONS ON
GAS-PHASE MERCURY OXIDATION BY
CHLORINE AND BROMINE**

Abstract

Bench-scale experiments were conducted in a 0.3 kW, quartz-lined, natural gas-fired reactor with the combustion air replaced with a blend of 27 mole % oxygen, with the balance carbon dioxide. Quench rates of 210 and 440 K/s were tested. In the absence of sulfur dioxide, the oxy-firing environment caused a remarkable increase in oxidation of mercury by chlorine. At 400 ppm chlorine (as HCl equivalent), air-firing resulted in roughly 5 % oxidation. At the same conditions with oxy-firing, oxidation levels were roughly 80 %. Oxidation levels with bromine at 25 and 50 ppm (as HBr equivalent) ranged from 80 to 95 % and were roughly the same for oxy- and air-firing conditions. Mixtures of 25 ppm bromine and 100 and 400 ppm chlorine gave more than 90 % oxidation. At all conditions, the effects of quench rate were not significant.

The presence of 500 ppm SO₂ caused a dramatic decline in the levels of oxidation at all oxy-fired conditions examined. This effect suggests that SO₂ may be preventing oxidation in the gas phase or preventing oxidation in the wet-conditioning system that was used in quantifying oxidized and elemental mercury concentrations. Similar effects of SO₂ have been noted with air-firing. The addition of sodium thiosulfate to the

hydroxide impingers that are part of wet conditioning systems may prevent liquid-phase oxidation from occurring.

Introduction

Previous studies of mercury emissions and their control in coal combustion systems have focused on homogeneous and heterogeneous oxidation of mercury by halogens in air-fired systems. Recent studies have also included the injection of bromine as a way to increase the amount of oxidized mercury and its removal in air pollution control devices. This study focuses on the gas-phase oxidation of mercury in oxygen-fired systems (oxy-fuel combustion). The interactions between mercury and other flue gas components in oxy-fired systems are largely unexplored. Oxy-firing of coal is of interest because of concerns over carbon dioxide emissions and global climate. Burning coal with oxygen and recycled combustion products is a technique that facilitates CO₂ capture and sequestration.

The fate and speciation of mercury in oxy-coal combustion processes is of particular interest because trace amounts of mercury lead to the embrittlement and cracking of aluminum heat exchangers that are used in the cryogenic separation and compression of carbon dioxide. Mercury exists in three forms in coal-derived flue gas: particle-bound (Hg^p), oxidized (Hg⁺⁺), and elemental (Hg⁰). The oxidized form is desirable because it is more readily removed by adsorption on solids and is more readily captured by absorption in wet flue gas desulfurization scrubbers. The adsorbed, particle-bound mercury captured by electrostatic precipitators (ESPs) or fabric filters.

Oxidized mercury is primarily mercuric chloride and bromide (HgCl₂ and HgBr₂) and their formation depend on the halogen content of the coal and the existence of

catalytic surfaces that enable oxidation. The latter includes unburned carbon and SCR reactors. This work focuses on the homogeneous, gas-phase oxidation of mercury by bromine and chlorine under oxy-firing conditions. There is a dearth of oxy-fired, mercury-oxidation results for homogeneous and heterogeneous conditions.

Previous work in this area includes Suriyawong et al. (1) who used oxygen-nitrogen or oxygen-carbon dioxide mixtures in an alumina tubular reactor with a peak temperature of 1200⁰C. A pulverized, western sub-bituminous coal was fed at 1 g/h. They found that 10 to 20 % of the mercury in the coal was oxidized and that the extent of mercury oxidation was unaffected by changing from air to oxy-firing.

Oxy-coal experiments conducted in a 1.5 MW facility (2) showed 75 % mercury removal across the electrostatic precipitator (ESP) with oxy-firing and 63 % with air-firing. The temperature of the ESP and the sulfur content of the coal were key factors affecting removal. Lower temperature and lower sulfur content led to higher removal. The recycle of flue gas in oxy-coal systems led to higher mercury concentrations at the inlet to the ESP.

The objective of this study was to determine how gas-phase mercury oxidation by bromine and chlorine is affected by a flue gas that is generated from burning methane with a mixture O₂/CO₂ instead of with air. The effects of SO₂ were included.

Experimental Section

The natural gas-fired, quartz-line mercury reactor is shown schematically in Figure 7.1 with associated equipment. The reactor consists of a 5-cm OD x 4.7-cm ID quartz tube (132 cm in length) located along the center of a high-temperature Thermcraft heater. The tube extends 79 cm below the heater, is temperature controlled, and has a

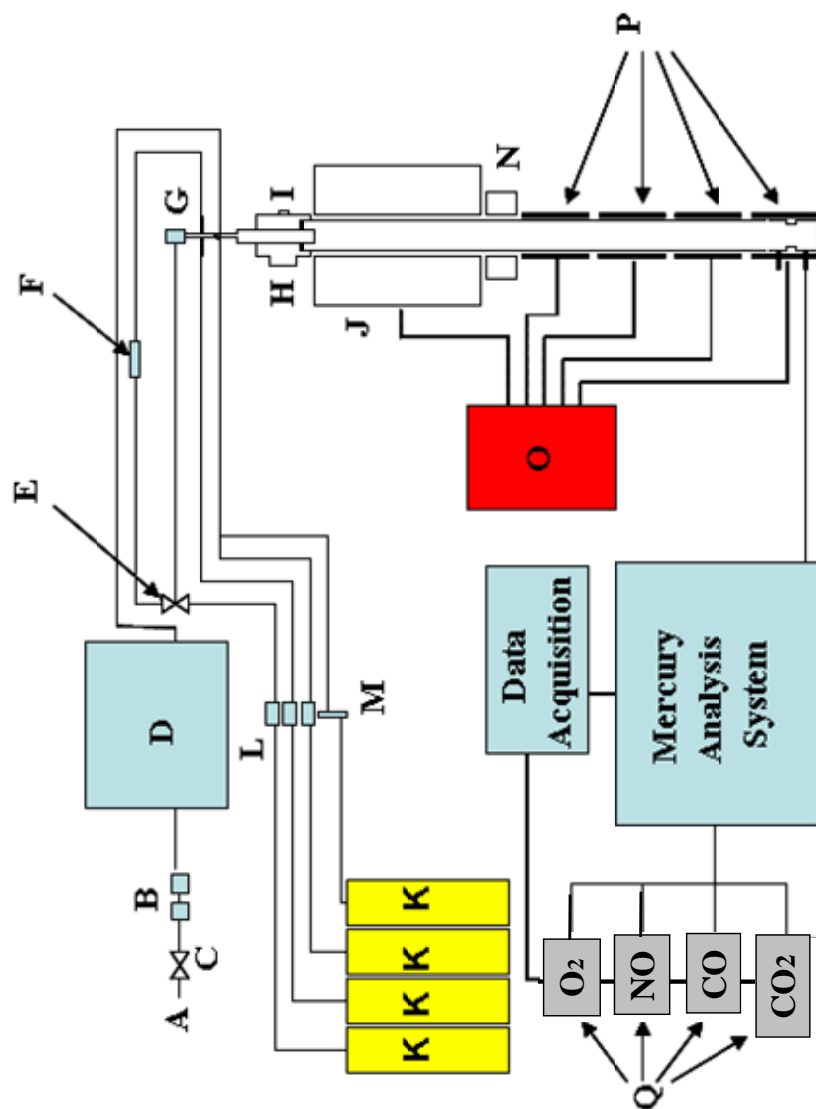


Figure 7.1. Mercury reactor. Adapted (3)

A: Compressed air, B: Filter, C: Pressure regulator, D: Mercury cal gas generator (CavKit), E: Solenoid valve, F: Flashback arrestor, G: UV valve, H: Support T and blow off nozzle, I: Purge nozzle, J: Thermocraft heater, K: Gas cylinders, L: Mass flow controllers, M: Rotameter, N: Inswool, O: Temperature controllers, P: Heating tapes, Q: Analyzers.

quartz sampling section attached at the bottom with a capped end. The peak gas temperature in the electrically heated zone was about 1080°C. The reactor was operated with two temperature profiles with quench rates of 210 and 440 K/s. The former will be referred to as low-quench (LQ) and the latter as high-quench (HQ).

The air-fired temperature profiles are given in Figure 7.2 and were obtained by adjusting the current supplied to the heaters surrounding the bottom 79 cm of the quartz tube. The effect of oxy-firing on temperatures and temperature profiles was not determined although temperatures should be slightly lower because of the higher heat capacity of CO₂ (37.3 J/mol-K at 300 K) relative to that of N₂ (29.1 J/mol-K at 300K).

A 300-W, methane-fired, premixed burner made of quartz glass supplied realistic combustion gasses to the reactor. All reactants were introduced through the burner and passed through the flame to create a radical pool representative of combustion systems. To study the effects of SO₂ and halogens, different concentrations of these were introduced through the burner.

For the oxy-fuel conditions the combustion air was replaced with a mixture of 27% O₂ and 73% CO₂. Bottled gas mixtures of 3000 ppm Br₂ in air, 6000 ppm Cl₂ in air, and 6000 ppm SO₂ in air were used as sources of the flue gas species. Depending on the amount of these gases added to the burner, the mole fraction of N₂ in the system varied from 0.7277 to 0.0036. A Tekran 2537A Mercury Analyzer, coupled with a wet sample conditioning system designed by Southern Research Institute (SRI), provided measurement of total and elemental mercury in the exhaust gas and is shown in Figure 7.3. In the baseline conditioning system, one stream was bubbled through a NH₂OH-HCl/NaOH solution to reduce all mercury to elemental form. This stream represented the

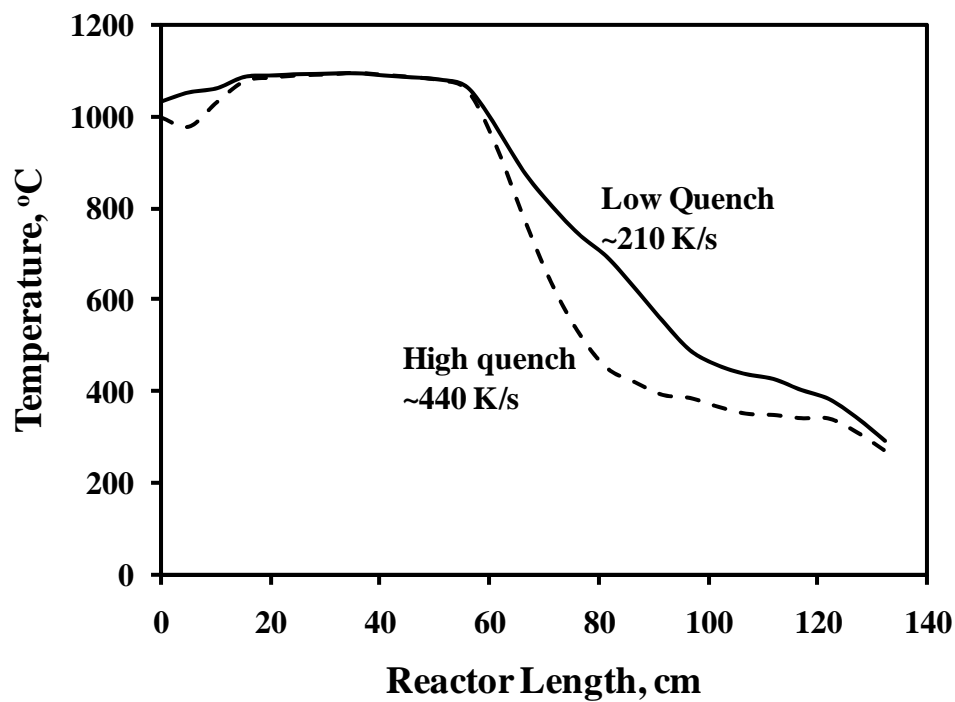


Figure 7.2. Temperature profiles.

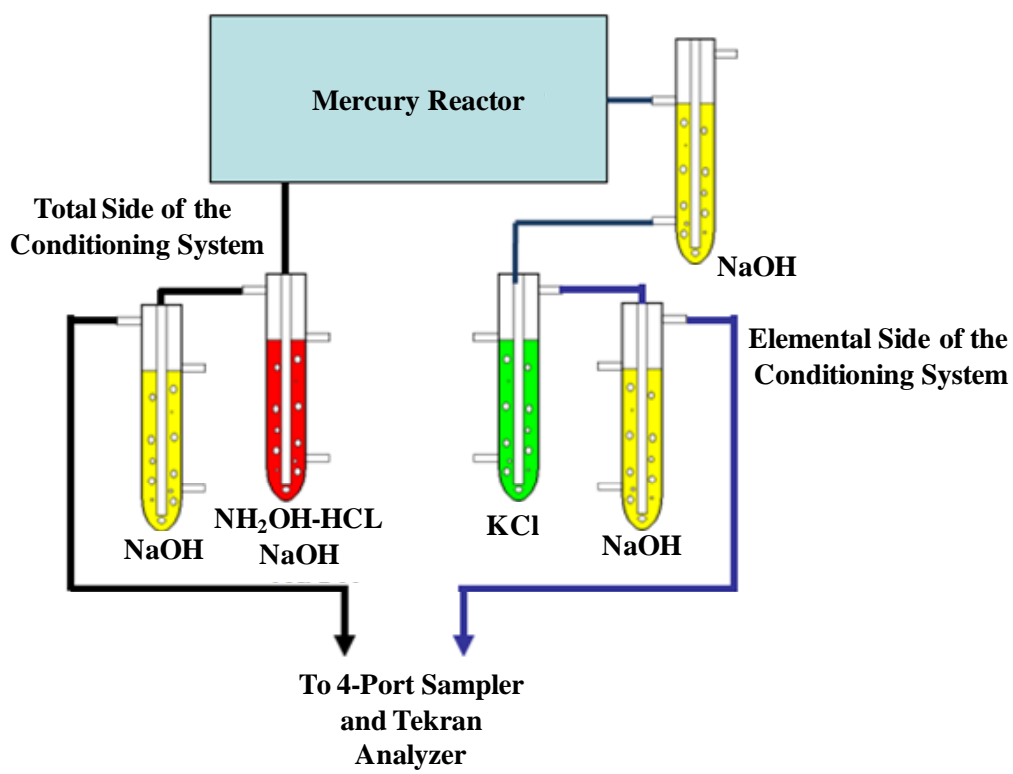


Figure 7.3. Conditioning system.

total mercury concentration present in the system. The other stream was passed first through a solution containing 5 wt % NaOH and then through 10 wt% KCl and 0.5 wt% $\text{Na}_2\text{S}_2\text{O}_3$ to capture oxidized mercury. Sodium thiosulfate was added to prevent oxidation of elemental mercury by halogens in solution (4). This stream represented the elemental mercury concentration present in the system. A 5 wt% NaOH solution was used to remove acid gases from each of the sample streams. The impingers had a flow-through arrangement on the liquid side, so that they were continually being refreshed. The two sample streams then passed through a chiller to remove any water. A Tekran 2537A mercury analyzer was used to measure the elemental mercury concentration of each stream. A four-port sampler controlled which stream the Tekran Analyzer sampled. The concentration of oxidized mercury was calculated from the difference between the total and elemental mercury stream concentrations. The experiments were performed with Br_2 and Cl_2 added through the burner. Before adding these, the baseline mercury level at the furnace outlet was checked using a material balance (see Figure 7.4). Because of limited resources, the experiments were performed just once.

Table 7.1 gives the baseline, air-fired flue gas composition for the experiments on a dry basis. The gas composition was not intended to duplicate the flue gas in coal-fired power plants; the intent of this work was to study reactions of mercury and common flue gas species in a well-controlled system. All species that were added to the reactor (SO_2 , Cl_2 , Hg^0 , and Br_2) passed through the flame. Their subsequent speciation depended on flame chemistry as well as on the temperature profile in the reactor. The effects of oxy-firing on flue-gas composition were not independently measured with gas analyzers as they were for the air-fired results in Table 7.1. For the oxy-fired experiments, the air was

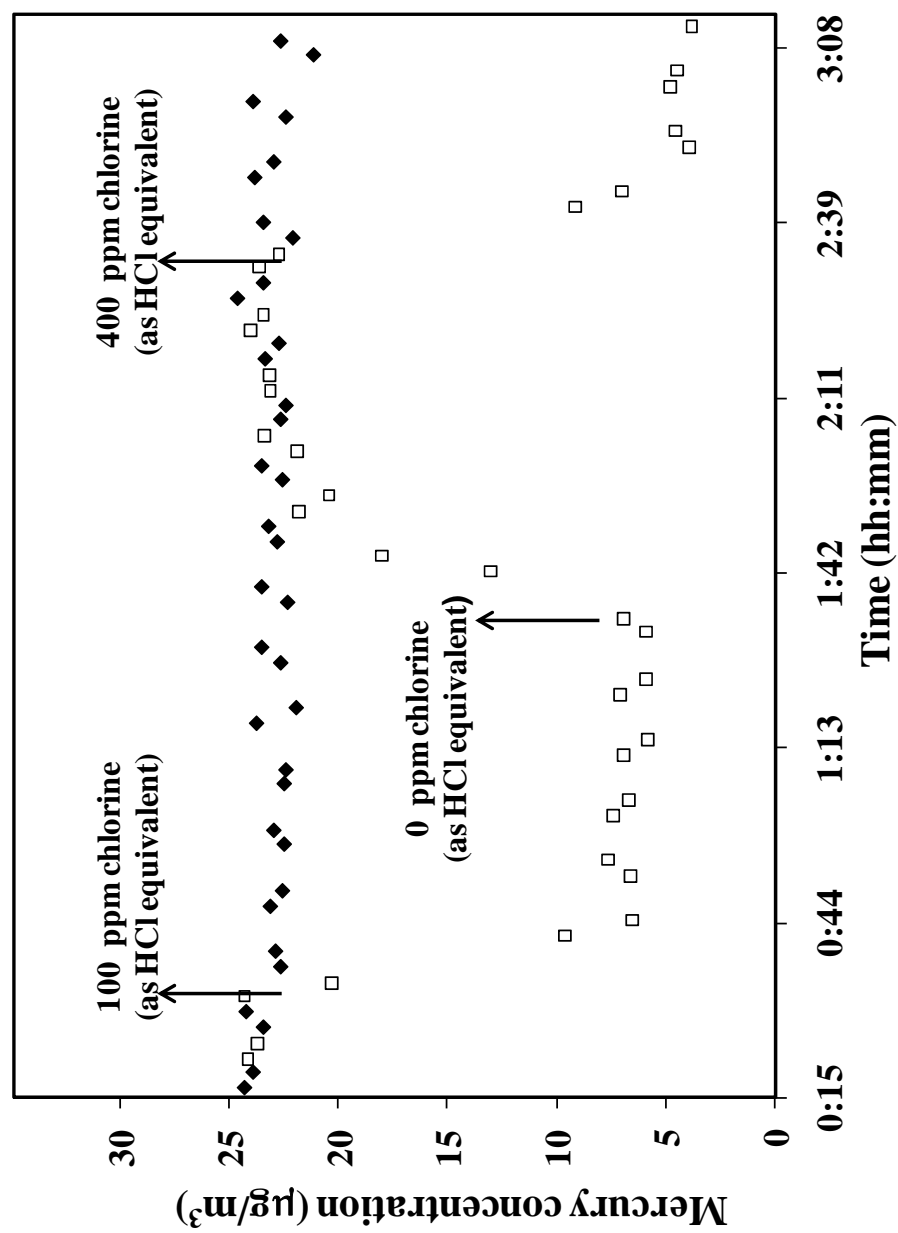


Figure 7.4. Sample of an experimental measurement from the analyzer.

Table 7.1. Flue gas composition for experiments.

Species	Concentration
O₂	0.8 vol. %
H₂O	16.5 vol %
CO₂	7.7 vol. %
NO	30- 500 ppm
SO₂*	0 - 500 ppm
HCL**	0 - 500 ppm
HBr***	0 - 50 ppm
Hg⁰	25 g/Nm ³

* Bottle composition 6000 ppm (SO₂) in air

** Assuming all chlorine added as HCL (bottle composition 6000 ppm Cl₂ in air).

*** Assuming all chlorine added as HBr (bottle composition 3000 ppm Br₂ in air).

replaced with a mixture of 27 % oxygen and 73 % CO₂, and the amount added was calculated to give the same oxygen level, 1.0 %, as in the air-fired tests. This mixture composition, 27 % O₂ and 73 % CO₂, was chosen to match typical industrial conditions. The concentration of NO_x was not measured and NO and NO₂ were not added to the reactor. The 30 ppm NO observed with air-firing was from the natural gas flame. The effects of NO and NO₂ on mercury oxidation in air-fired tests were negligible (5).

Results and Discussion

Typical air-fired, gas-phase oxidation results with the high-quench profile and a baseline mercury concentration of 25 µg/m³ are shown in Figure 7.5. Bromine is clearly a superior oxidant at these conditions with oxidation levels ranging from 30 to 80 % at bromine concentrations ranging from 20 to 50 ppm bromine (as HBr equivalent). The

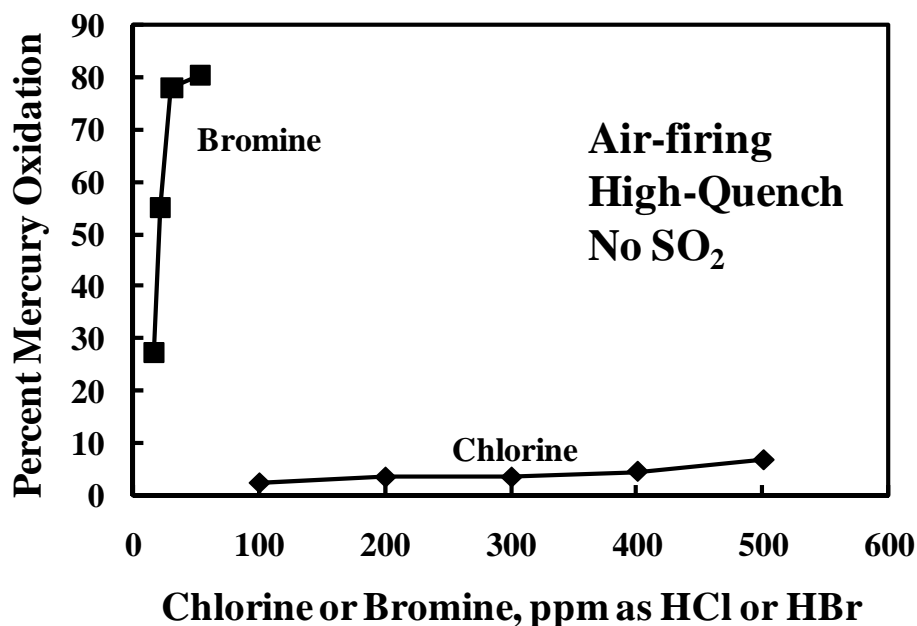


Figure 7.5. Extents of oxidation by bromine and chlorine with air-firing and no SO_2 .

extent of oxidation by chlorine ranges from 2 to 7 % at 100 to 500 ppm chlorine (as HCl equivalent). The results in Figure 7.5 were obtained in the absence of SO_2 .

Effects of Oxy-firing on Gas-phase Mercury Oxidation by Chlorine and Bromine

Replacement of the combustion air with a mixture of 27 % oxygen, balance carbon dioxide, had a dramatic effect on the ability of chlorine to oxidize mercury. Figure 7.6 shows gas-phase oxidation levels with oxy-firing of 70 to 80 % at 100 and 400 ppm chlorine (as HCl equivalent). Oxidation levels with bromine at 25 and 50 ppm (as HBr equivalent) range from 70 to 100 %. The results in Figure 7.6 were obtained in the absence of SO_2 .

Figure 7.7 shows measured gas-phase oxidation levels with oxy-firing as a function of quench rate and bromine concentrations. The levels of oxidation are insensitive to quench rate and range from 75 to 100 percent as bromine concentration is

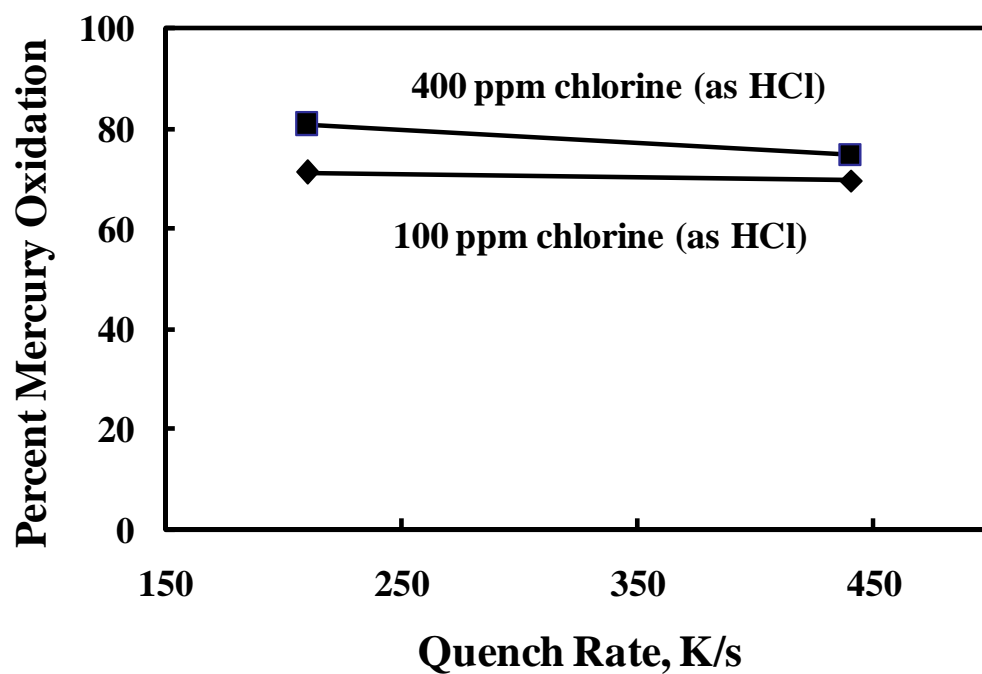


Figure 7.6. Extents of oxidation with oxy-firing, chlorine, and no SO₂.

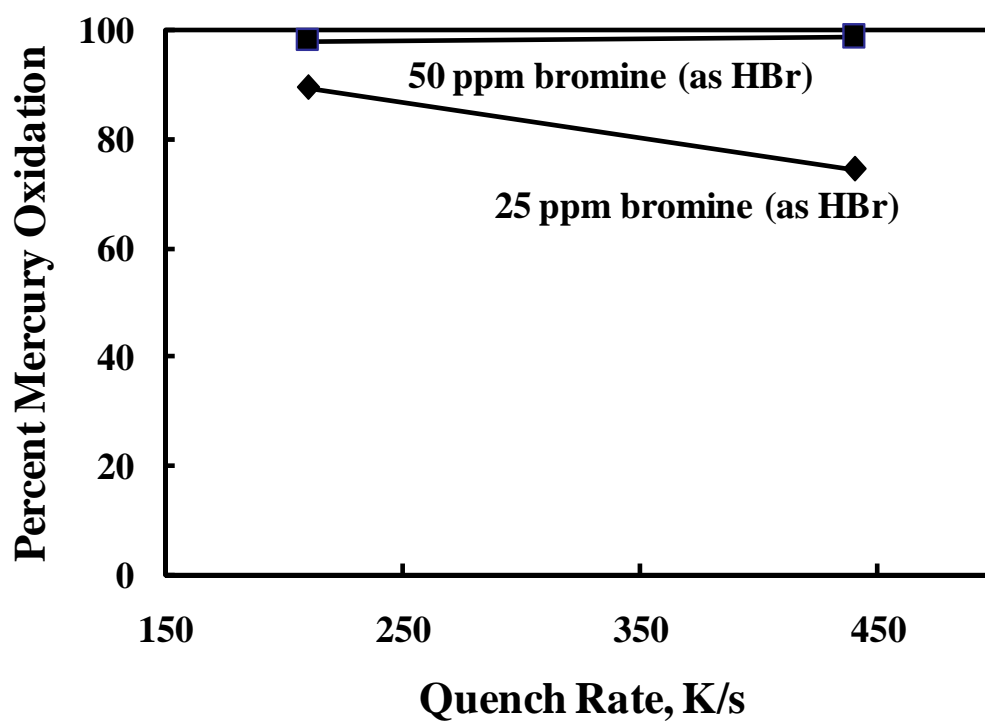


Figure 7.7. Experimental results of the oxidation of elemental mercury with oxy-firing, bromine, and no SO₂.

increased from 25 to 50 ppm (as HBr equivalent).

The effects of mixtures of bromine and chlorine with oxy-firing on oxidation are shown in Figure 7.8. The presence of 25 ppm bromine (as HBr equivalent) and chlorine concentrations from 100 to 400 ppm (as HCl equivalent) resulted in higher levels of oxidation than when just bromine or chlorine was present. Changing the concentration from 100 to 400 ppm had no effect on levels of oxidation.

Effect of SO₂

The results in Figures 7.5 to 7.8 were obtained in the absence of SO₂. At 500 ppm SO₂, the oxy-fired results in Figures 7.5 to 7.8 are replaced with the results in Figure 7.9. The ability of chlorine and bromine to oxidize mercury drops dramatically. A mechanistic explanation of these results may involve gas-phase reactions between the halogens and SO₂.

A second explanation involves aqueous-phase reactions that are interfering with the conditioning system used to determine mercury concentrations. It is possible that the aqueous reactions can be controlled by adding reducing agents such as sodium thiosulfate to the sodium hydroxide impinger solutions. The results in Figure 7.5 to 7.8 may be associated to oxidation of elemental mercury in those impingers. The KCl impinger solution is already treated with sodium thiosulfate (4) to prevent halogens from oxidizing mercury. Sulfur dioxide also acts as a reducing agent, hence, the hypothesis that the results in Figure 7.9 are an artifact of the wet conditioning system.

The results of Suriyawong et al. (1) and Imada et al. (2) show little impact of oxy-firing on the oxidation of mercury in coal-fired systems. In those studies, heterogeneous reactions were probably important. Our data suggest that when heterogeneous reactions

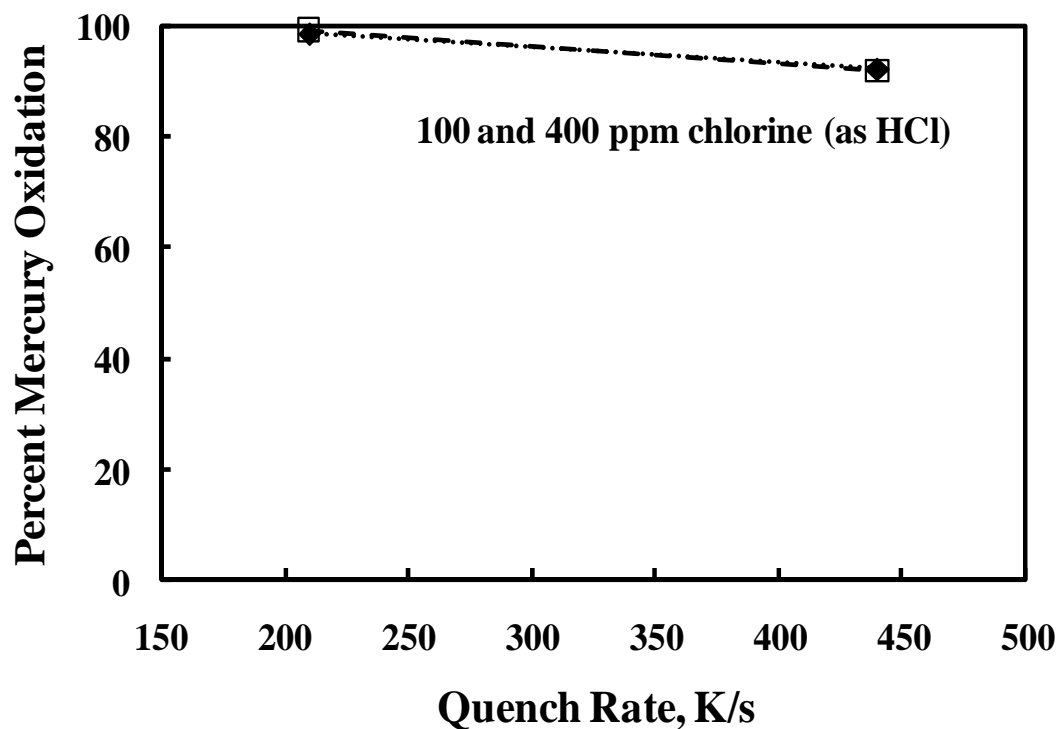


Figure 7.8. Experimental results of the mercury oxidation with oxy-firing, mixtures of bromine and chlorine, and no SO_2 .

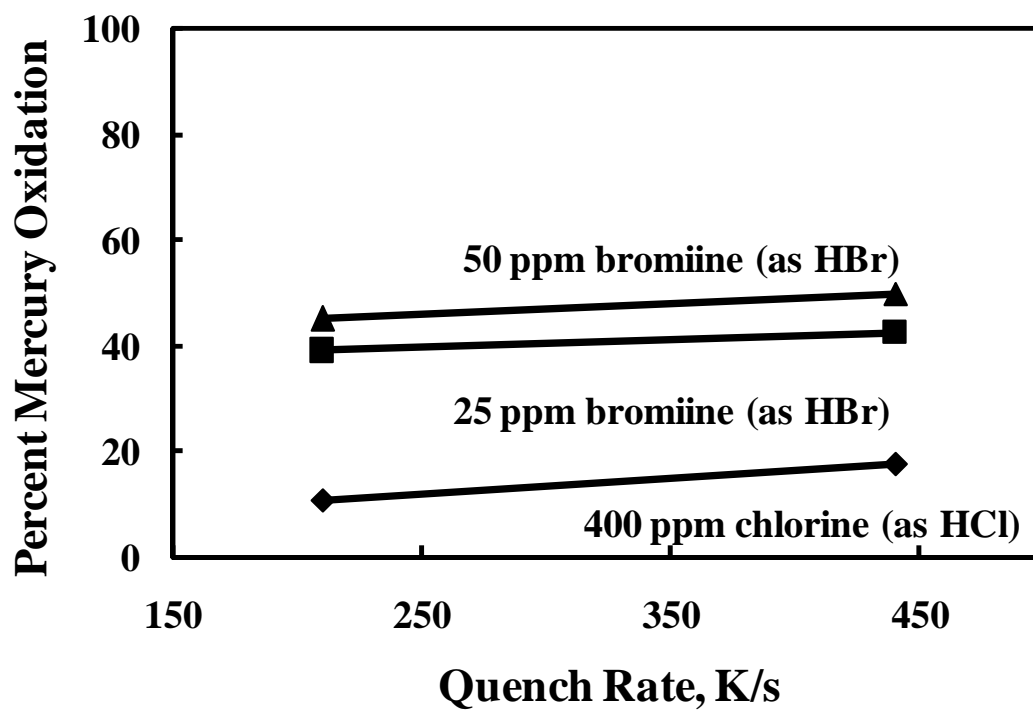


Figure 7.9. Mercury oxidation with oxy-firing, mixtures of bromine and chlorine, in the presence of SO_2 .

are excluded, oxy-firing also has little effect on gas-phase oxidation by halogens, except when chlorine is present in the system. In this case, the oxidation is significantly higher than the observed under air-firing conditions.

Conclusions

Bench-scale experiments were conducted in the University of Utah's quartz-lined, natural gas-fired reactor with the combustion air replaced with a blend of 27 mole % oxygen and 73 % carbon dioxide. In the absence of sulfur dioxide, the oxy-firing environment caused an increase in oxidation of mercury by chlorine. At 400 ppm chlorine (as HCl equivalent), air-firing results in roughly 5 % oxidation. At the same conditions with oxy-firing, oxidation levels are roughly 80 %. Oxidation levels with bromine at 25 and 50 ppm (as HBr equivalent) ranged from 80 to 95 % and were roughly the same for oxy- and air-firing conditions.

The presence of 500 ppm SO₂ caused a dramatic decline in the levels of oxidation at all oxy-fired conditions examined. This effect suggests that SO₂ may be preventing oxidation in the gas phase or preventing oxidation in the wet-conditioning system that was used in quantifying oxidized and elemental mercury concentrations. Similar effects of SO₂ have been noted with air-firing. The addition of sodium thiosulfate to the hydroxide impingers that are part of wet conditioning systems may prevent liquid-phase oxidation from occurring.

References

1. Suriyawong, A., Gamble, M., Lee, M., Axelbaum, R., Biswas, P. Submicrometer Particle Formation and Mercury Speciation under O₂-CO₂ Coal Combustion. *Energy & Fuels* **2006**, 20, 2357-2363.
2. Imada, N., Kikkawa, K., Kobayashi, N. *Study of Mercury Behavior in Flue Gas of Oxy-fuel Combustion*. The 35th International Technical Conference on Clean Coal & Fuel Systems, Clearwater, Florida, June 2010.
3. Fry, A.; Cauch, B.; Silcox, G.; Lighty, J.; Senior, C. *Experimental Evaluation of the Effects of Quench Rate and Quartz Surface Area on Homogeneous Mercury Oxidation*. 31st International Symposium on Combustion, Heidelberg, Germany, August, 2006.
4. Cauch, B.; Silcox, G.; Lighty, J.; Wendt, J.; Fry, A.; Senior, C. Confounding Effects of Aqueous-Phase Impinger Chemistry on Apparent Oxidation of Mercury in Flue Gases. *Environ. Sci. Technol.* **2008**, 42(7), 2594–2599.
5. Fry, A. Experimental and Kinetic Modeling Investigation of Gas-Phase Mercury Oxidation Reactions with Chlorine. Ph.D Diss. University of Utah, 2008.

CHAPTER 8

OVERALL CONCLUSIONS AND RECOMMENDATIONS

Mercury oxidation was studied under simulated flue-gas conditions by tracking the changes on elemental mercury when experimental conditions were modified in a quartz tubular reactor. This study demonstrated, through both experiments and model, the major impacts of temperature and typical flue gases such as chlorine, SO₂ and bromine on mercury oxidation. Several important contributions can be extracted from this work. First, the individual and simultaneous effect of the species stated above on mercury oxidation constituted one of the first studies of this type; second, the extensive work on the conditioning system allowed identifying new experimental arrangements to improve the actual methods for elemental and total mercury measurements; third, this study presented new data on mercury oxidation under oxy-fuel fired conditions, which has not been presented before. Finally, the experimental and modeling results represent an important source of comparison and validation for other studies.

Specifically, this work showed that:

Mercury speciation in simulated flue gases depended on the temperature profile used in the reactor as well as on the composition of the flue gas. Under the temperature and composition conditions of this study, species such as chlorine and SO₂ did not have a significant impact on mercury oxidation. In contrast, bromine had a strong impact on the extent of mercury oxidized resulting in oxidations higher than 90 % in presence of 50

ppm bromine (as HBr equivalent). The effect of bromine on mercury oxidation was more pronounced under the low-quench temperature profile than the high-quench temperature profile.

The SO_2 had an inhibitory effect on mercury oxidation by bromine. It was found that this effect was mostly due to liquid phase interactions inside the impingers on the elemental side of the conditioning system. This bias on elemental mercury measurements by the wet conditioning system was corrected by installing a NaOH impinger prior the potassium chloride impinger. This additional impinger removed the SO_2 before it enters the KCl impinger eliminating the possibility of liquid phase reactions. With this new configuration there is no effect of SO_2 on mercury oxidation by bromine due to gas phase interactions when the SO_2 concentration is higher than 200 ppm.

The simultaneous presence of bromine and SO_2 also generated a bias on the total mercury concentration measurements. A decrease in concentration was observed when both species were present in the system. This bias was significantly decreased using a hydroxylamine hydrochloride-sodium hydroxide solution instead of the usual stannous chloride- hydrochloric acid solution to reduce the oxidized mercury to its elemental form.

Mercury oxidation by bromine was slightly increased by the presence of chlorine. This increase was roughly dependent on the chlorine concentration and the temperature profile along the reactor. It was observed that a higher chlorine concentration resulted in a higher mercury oxidation. The extent of mercury oxidation was also higher for the low-quench temperature profile compared to the high-quench profile.

In contrast to the negligible effect that chlorine had on mercury oxidation under air-firing conditions, the extent of mercury oxidation by chlorine was considerably higher

under oxy-fuel conditions for the two temperature profiles used in this study. A slight increase in mercury oxidation by bromine was also observed under oxy-fuel conditions. It was difficult to determine the effect of the simultaneous presence of bromine and chlorine on mercury oxidation under oxy-fuel conditions because the extent of mercury oxidation under these conditions was nearly 100% even at bromine concentrations as low as 25 ppm.

The SO_2 did not affect mercury oxidation under oxy-fuel conditions; however it had a strong inhibitory effect on mercury oxidation by bromine and chlorine.

Recommendations for Future Work

This dissertation included important findings about the optimization of mercury measurements in presence of flue gas components of great interest for the mitigation of mercury emissions, such as bromine and SO_2 . It was demonstrated that in some cases the effect of halogens or acid gases on mercury oxidation could be explained by liquid phase chemistry rather than gas phase interactions. The techniques implemented in this work allowed the decrease or in some case the complete elimination on the bias or deviations in mercury measurements.

Additional to the optimization of the mercury measurements, a new combustion method was incorporated into the experimental conditions. In this new method, the oxy fuel combustion, methane was burned with a mixture O_2/CO_2 instead of air. These combustion conditions offered a favorable environment for mercury oxidation by chlorine. Again, care should be taken in determining the extent of mercury oxidation generated from liquid phase interactions. A significant portion of the elemental mercury was oxidized by SO_2 under oxy fuel conditions. The removal of the SO_2 prior to entering

the conditioning system showed that mercury oxidation was a product of liquid phase interactions inside the conditioning system rather than gas phase interactions.

Based on the high impact that interactions inside the conditioning system had in the mercury measurements done in this work, it is recommended to focus future experimental efforts on the development and implementation of dry methods to measure mercury speciation under simulated flue gas conditions as well as on the study of liquid phase interactions occurring inside the NaOH impinger in the wet conditioning system configuration.

An important amount of the experimental work for this dissertation was focused on the optimization of a system to study heterogeneous mercury oxidation and adsorption. Pressure drop and leak problems were solved but the obtained experimental data did not agree with the typical adsorption capacities reported in previous studies for the same activated carbons. This might be associated with the difference in experimental setups. Therefore, it is recommended to simulate the flue gas by injecting calibration gases instead of the methane flame and determine the adsorption capacities at different initial concentrations of elemental mercury. This will be helpful for identifying the effect of water vapor and other components from the combustion process on mercury adsorption and mercury oxidation.

APPENDIX A

MODIFICATIONS TO THE CONDITIONING SYSTEM TO STUDY IMPINGER CHEMISTRY

For mercury analysis, two sample streams were taken from the bottom of the reaction chamber and introduced into a wet-chemical conditioning system, shown in Figure 5.2. In the baseline conditioning system, one stream was bubbled through an acidic 2% SnCl_2 solution to reduce all mercury to elemental form. This stream represented the total mercury concentration present in the system. The other stream was passed through a solution containing 10 wt% KCl and 0.5 wt% $\text{Na}_2\text{S}_2\text{O}_3$ to capture oxidized mercury. Sodium thiosulfate was added to prevent oxidation of elemental mercury by halogens in solution (8). This stream represented the elemental mercury concentration present in the system. A 5 wt% NaOH solution was used to remove acid gases from each of the sample streams. The impingers had a flow-through arrangement on the liquid side, so that they were continually being refreshed. The two sample streams then passed through a chiller to remove any water. The baseline configuration of the conditioning system is shown in Figure A.1.

Total Side of the Conditioning System

To determine if the bromine compounds produced in the reactor are affecting the chemistry in the impingers on the total side of the flue gas conditioning system, different

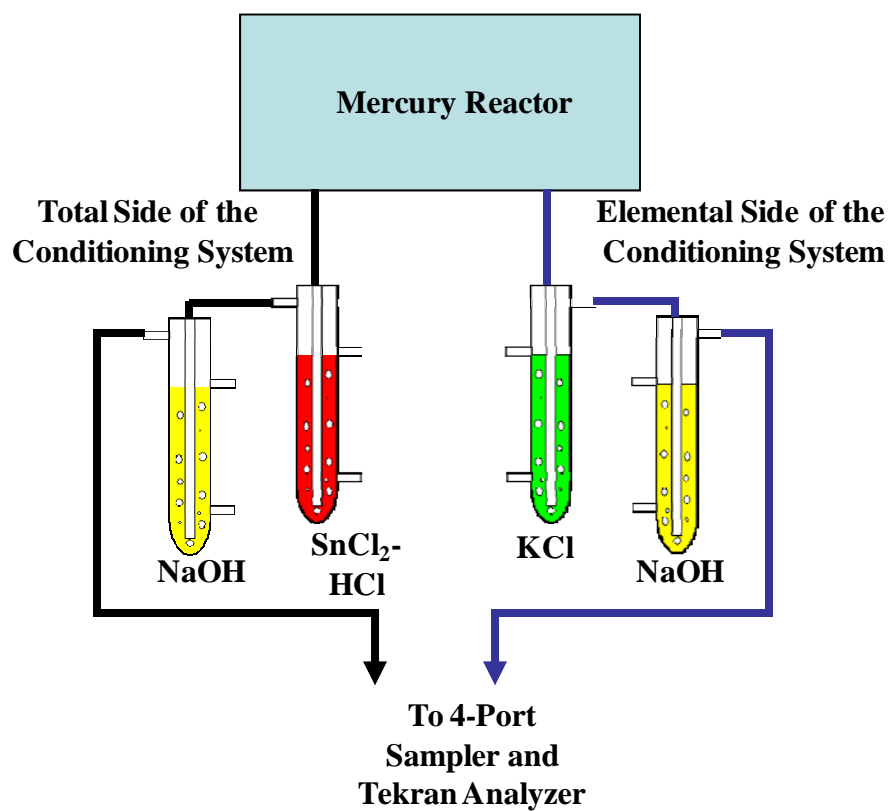


Figure A.1. Usual configuration of the conditioning system.

impinger solutions are evaluated. The usual configuration for the total side is an impinger containing 2 wt% SnCl_2 and 3 wt% HCl in water, followed by an impinger containing NaOH . The solution in the first impinger is modified or, in some cases, additional impingers are added to improve the reduction from total to elemental mercury. Some of these modifications include the increase or decrease in the concentration of the SnCl_2 - HCl solution, the addition of one or two NaOH impingers before the SnCl_2 - HCl impinger (Figure A.2) and the substitution of the SnCl_2 - HCl solution by a mixture of hydroxylamine hydrochloride and sodium hydroxide ($\text{NH}_2\text{OH}\cdot\text{HCl}$ - NaOH) (Figure A.3).

Elemental Side of the Conditioning System

To determine if the measurements on the elemental side of the conditioning system are affected by the bromine species in the reactor, different impinger solutions were evaluated as well. The default configuration for the elemental side was an impinger containing 10 wt % KCl and 0.5 wt % sodium thiosulfate in water, followed by an impinger containing NaOH . The solution in the first impinger is modified or, in one case, the first impinger is eliminated and only the NaOH impinger is used on the elemental mercury side. To determine the overall effect of the SO_2 on mercury oxidation by bromine, some measurements of the SO_2 concentration along the reactor in both gas and liquid phases is made; these results are an indication of the points of the system where the highest SO_2 consumption is taking place and in which phase the highest interaction between oxidized mercury and SO_2 species could be taking place.

The solutions in the first impinger that were tested included (1) the standard configuration of 10 wt% KCl and 0.5 wt% sodium thiosulfate in water, followed by an

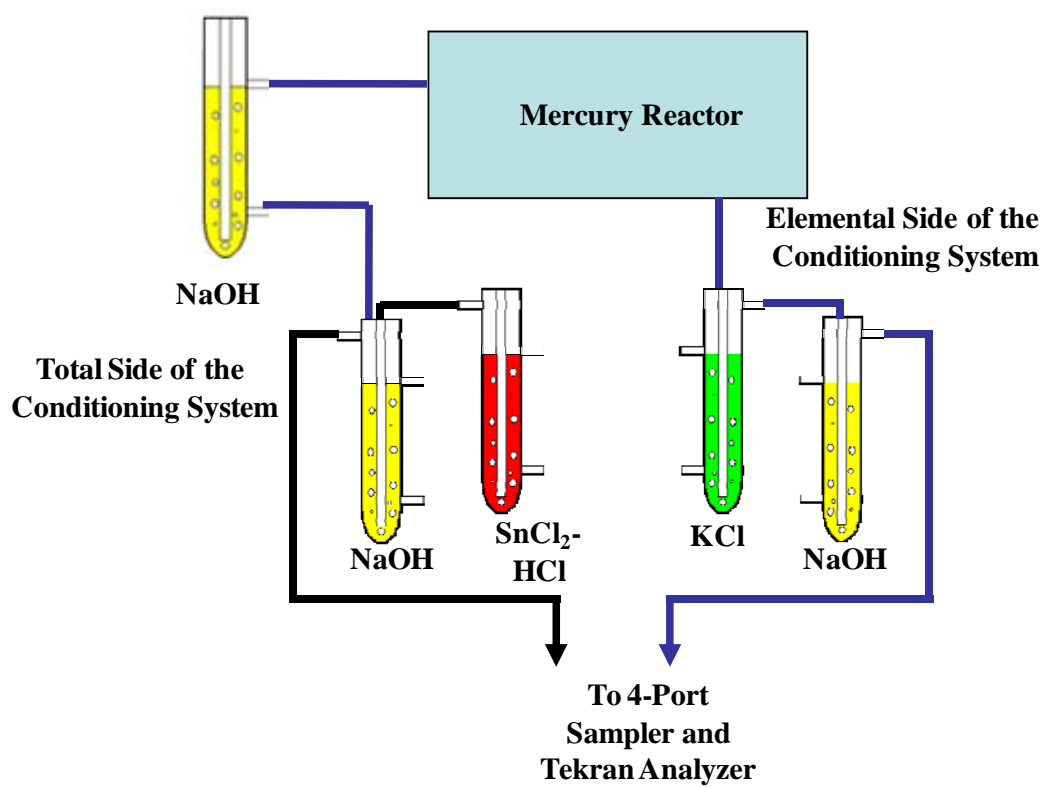


Figure A.2. Additional impingers on the total side of the conditioning system.

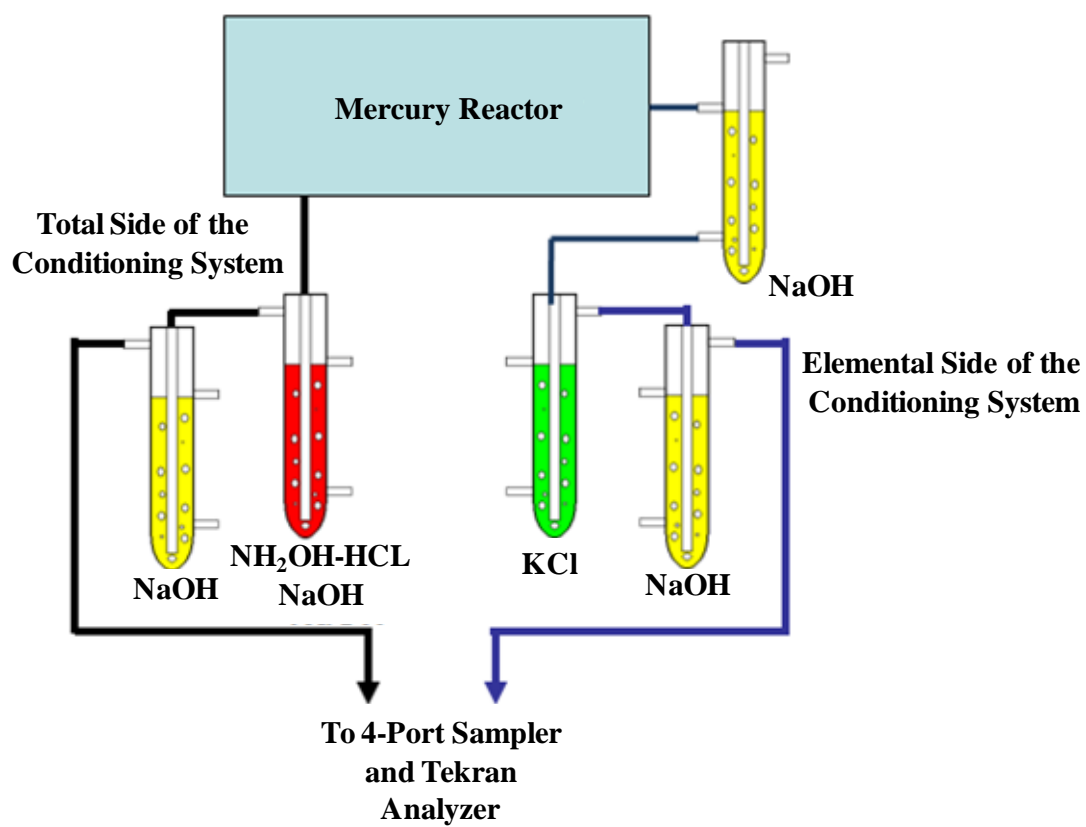


Figure A.3. Additional impingers on the elemental side of the conditioning system.

impinger 5 wt % NaOH; (2) the standard configuration without the sodium thiosulfate; (3) replacement of the KCl and sodium thiosulfate with 12 wt % of tris (hydroxymethyl) aminomethane (THAM) and 0.3 wt % ethylenediamine tetra acetic acid (EDTA); and (4) a single impinger containing 5 wt % sodium hydroxide.

The elemental side of the conditioning system was also modified by the addition of one impinger or, in some cases, a packed bed to further study mercury-bromine-SO₂ interactions that could be occurring in the conditioning system. The default configuration for the elemental side was an impinger containing 10 wt% KCl and 0.5 wt% sodium thiosulfate in water, followed by an impinger containing NaOH, as shown in Figure A.1. The modifications implemented were (1) an additional impinger of a 5 wt % NaOH solution before the KCl impinger in the standard configuration (Figure A.4), (2) a bed with 2 grams of hydrated lime at 120⁰C (Figure A.5) (3). The objective of these modifications was to remove the SO₂ before it reaches the KCl impinger; this was helpful in determining if any extent of the inhibitory effect of SO₂ on mercury oxidation by bromine was occurring in the liquid phase.

The temperature of this bed which was increased up to 500°C was expected to increase SO₂ adsorption. However it did not show that effect.

To avoid liquid phase interactions among bromine, mercury and SO₂, a packed bed with 40 grams of NaOH pellets heated at 120°C was installed just before the KCl impinger. The results were inconclusive and not reproducible due to the interaction of the NaOH with the quartz frit installed in the packed bed to support the pellets.

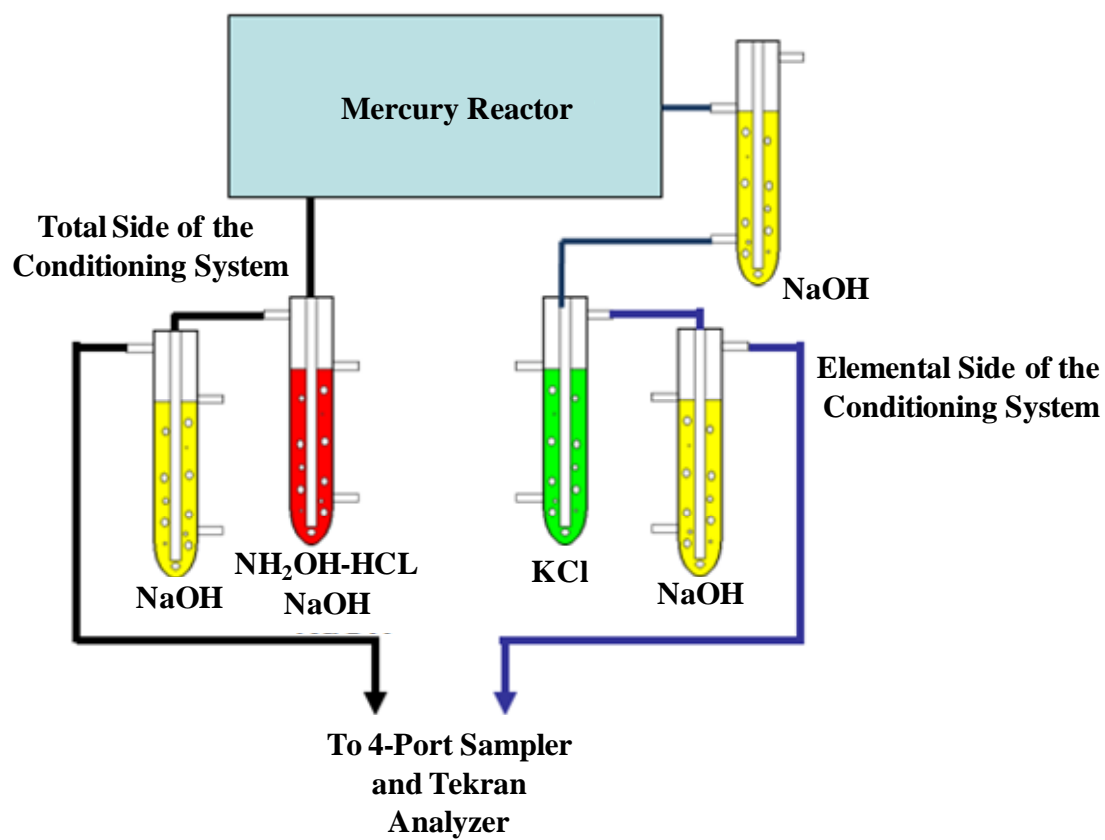


Figure A.4. Additional impinger of a 5 wt % NaOH solution before the KCl impinger in the standard configuration.

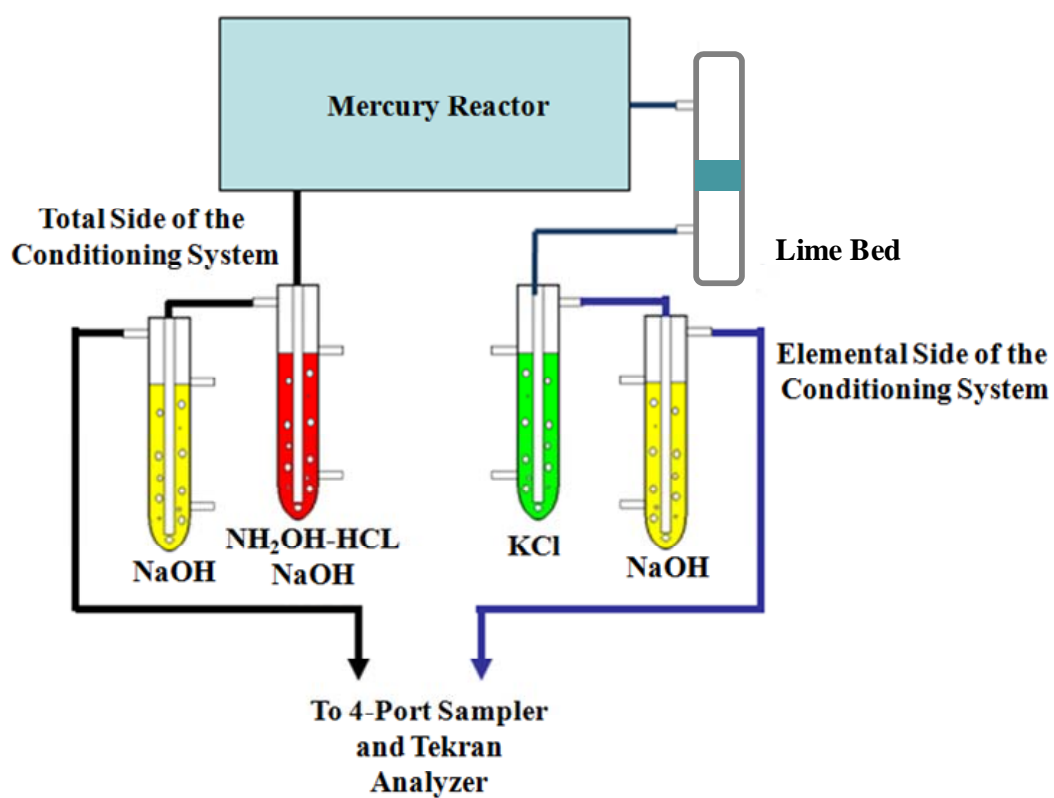


Figure A.5. Packed bed with 1 g of hydrated lime heated at 150⁰C. The same experimental setup was used for the NaOH pellets bed.

APPENDIX B

EXAMPLE OF CHEMKIN 4.1 INPUT PARAMETERS

Mercury Oxidation by 400 ppm Chlorine under Air firing Conditions and the High Quench Temperature Profile

Input parameters

MOMEN ON ! Turn on Momentum Equation
PLUG ! Plug Flow Reactor
RTIME ON ! Turn on Residence Time Calculation
TGIV ! Fix Gas Temperature
!Surface_Temperature ! Surface Temperature Same as Gas Temperature
PRES 0.85 ! Pressure (atm)
TPRO 0.0 1271.0 ! Temperature (K)
TPRO 5.08 1251.0 ! Temperature (K)
TPRO 10.16 1304.0 ! Temperature (K)
TPRO 15.24 1350.0 ! Temperature (K)
TPRO 20.32 1358.0 ! Temperature (K)
TPRO 25.4 1363.0 ! Temperature (K)
TPRO 30.48 1365.0 ! Temperature (K)
TPRO 35.56 1368.0 ! Temperature (K)
TPRO 40.64 1364.0 ! Temperature (K)
TPRO 45.72 1359.0 ! Temperature (K)
TPRO 50.8 1352.0 ! Temperature (K)
TPRO 55.88 1330.0 ! Temperature (K)
TPRO 60.96 1214.0 ! Temperature (K)
TPRO 66.04 1057.0 ! Temperature (K)
TPRO 71.12 913.0 ! Temperature (K)
TPRO 76.2 802.0 ! Temperature (K)
TPRO 81.28 726.0 ! Temperature (K)
TPRO 86.36 695.0 ! Temperature (K)
TPRO 91.44 667.0 ! Temperature (K)
TPRO 96.52 660.0 ! Temperature (K)
TPRO 101.6 641.0 ! Temperature (K)
TPRO 106.68 626.0 ! Temperature (K)
TPRO 111.76 623.0 ! Temperature (K)
TPRO 116.84 616.0 ! Temperature (K)

TPRO 121.92 615.0 ! Temperature (K)
TPRO 127.0 585.0 ! Temperature (K)
TPRO 132.08 545.0 ! Temperature (K)
VDOT 408.5 ! Volumetric Flow Rate (cm³/sec)
DIAM 4.699 ! Diameter (cm)
XEND 132.08 ! Ending Axial Position (cm)
REAC AR 0.0 ! Reactant Fraction (mole fraction)
REAC C 4.2256139988E-8 ! Reactant Fraction (mole fraction)
REAC C2H 5.1926239836E-9 ! Reactant Fraction (mole fraction)
REAC C2H2 8.0618376471E-7 ! Reactant Fraction (mole fraction)
REAC C2H3 7.4437805329E-8 ! Reactant Fraction (mole fraction)
REAC C2H4 9.7729383123E-7 ! Reactant Fraction (mole fraction)
REAC C2H5 1.220924515E-7 ! Reactant Fraction (mole fraction)
REAC C2H6 4.110767451E-7 ! Reactant Fraction (mole fraction)
REAC CH 1.6027200088E-7 ! Reactant Fraction (mole fraction)
REAC CH2 1.2292378039E-6 ! Reactant Fraction (mole fraction)
REAC CH2CO 3.9997183315E-7 ! Reactant Fraction (mole fraction)
REAC CH2O 6.0600797671E-6 ! Reactant Fraction (mole fraction)
REAC CH2OH 1.293280919E-7 ! Reactant Fraction (mole fraction)
REAC CH3 1.4795601721E-5 ! Reactant Fraction (mole fraction)
REAC CH3O 7.1029356847E-9 ! Reactant Fraction (mole fraction)
REAC CH3OH 1.0541455694E-7 ! Reactant Fraction (mole fraction)
REAC CH4 3.7532960248E-5 ! Reactant Fraction (mole fraction)
REAC CL 0.00039988 ! Reactant Fraction (mole fraction)
REAC CL2 0.0 ! Reactant Fraction (mole fraction)
REAC CO 1.9500376158E-5 ! Reactant Fraction (mole fraction)
REAC CO2 0.07951097 ! Reactant Fraction (mole fraction)
REAC H 0.00209988 ! Reactant Fraction (mole fraction)
REAC H2 0.00614609 ! Reactant Fraction (mole fraction)
REAC H2O 0.1688624 ! Reactant Fraction (mole fraction)
REAC H2O2 1.4489754794E-7 ! Reactant Fraction (mole fraction)
REAC HCCO 1.4084353664E-7 ! Reactant Fraction (mole fraction)
REAC HCCOH 1.7347063005E-8 ! Reactant Fraction (mole fraction)
REAC HG 2.3482045068E-9 ! Reactant Fraction (mole fraction)
REAC HNO 1.1564708671E-8 ! Reactant Fraction (mole fraction)
REAC HO2 3.0716063284E-6 ! Reactant Fraction (mole fraction)
REAC N 2.2025084138E-8 ! Reactant Fraction (mole fraction)
REAC N2 0.72770016 ! Reactant Fraction (mole fraction)
REAC N2O 1.4189039525E-7 ! Reactant Fraction (mole fraction)
REAC NH 1.0369031922E-8 ! Reactant Fraction (mole fraction)
REAC NO 3.6948081142E-5 ! Reactant Fraction (mole fraction)
REAC NO2 3.1284651198E-8 ! Reactant Fraction (mole fraction)
REAC O 0.00065788 ! Reactant Fraction (mole fraction)
REAC O2 0.00837387 ! Reactant Fraction (mole fraction)
REAC OH 0.00612597 ! Reactant Fraction (mole fraction)
REAC SO2 0.0 ! Reactant Fraction (mole fraction)

! Number of Continuation 0 ! Continuation Count
END

APPENDIX C

SUMMARY OF EXPERIMENTAL RESULTS

Table C.1. Effect of chlorine on mercury oxidation.

Chlorine ppmv	% Hg Oxidation (average)	Error Bars	
		Maximum	Minimum
100	2.31	0.08	0.08
200	3.38	0.20	0.20
300	3.66	0.38	0.36
400	5.07	0.71	0.55
500	6.32	0.60	0.94

Table C.2. Effect of chlorine and 500 ppm SO₂ on mercury oxidation.

Chlorine ppmv	% Hg oxidation (average)	Error bars	
		Minimum	Maximum
100	1.85	0.15	0.77
200	2.67	0.03	0.75
300	3.11	0.47	0.75
400	3.46	0.70	0.29
500	5.12	0.96	0.58

Table C.3. Effect of bromine and SO₂ on mercury oxidation.

Configuration of the Elemental Side of the Conditioning System	SO ₂ , bromine (ppm)	% Hg Oxidation	Error bars	
			Maximum	Minimum
Usual Configuration	50 ppm Br	74.68	5.4	6.07
KCl impinger without thiosulfate	50 ppm Br-500 ppm SO ₂	29.96	7.16	3.96
	50 ppm Br	75.95	0.71	0.22
THAM/EDTA solution	50 ppm Br-500 ppm SO ₂	32.63	0.31	0.62
	50 ppm Br	75.72	0.26	2.03
Only a NaOH impinger	50 ppm Br-500 ppm SO ₂	25.62	0.56	1.03
	50 ppm Br	76.54	0.25	1.47
	50 ppm Br-500 ppm SO ₂	27.19	1.25	0.77

Mercury Oxidation in Presence of Bromine and Chlorine

Bromine added as HBr equivalent

Chlorine added as HCl equivalent

Table C.4. High quench temperature profile.

Conditions	% Hg Oxidation (average)	PLOT	
		MAX	MIN
Chlorine (100 ppm)	2.31	0.08	0.08
Chlorine (400 ppm)	5.07	0.71	0.55
Bromine (25 ppm)	33.35	3.30	1.66
Bromine (25 ppm)+ Chlorine (100 ppm)	35.48	2.28	3.44
Bromine (25 ppm)+ Chlorine (400 ppm)	38.05	2.03	2.80
Bromine (50 ppm)	61.87	2.91	3.24
Bromine (50 ppm)+ Chlorine (100 ppm)	64.28	3.61	5.08
Bromine (50 ppm)+ Chlorine (400 ppm)	69.79	6.69	3.69

Table C.5. Low quench temperature profile.

Conditions	% Hg Oxidation (average)	PLOT	
		MAX	MIN
Chlorine (100 ppm)	5.31	0.84	1.08
Chlorine (400 ppm)	9.07	1.71	0.35
Bromine (25 ppm)	56.80	10.59	6.52
Bromine (25 ppm)+ Chlorine (100 ppm)	66.76	2.70	1.81
Bromine (25 ppm)+ Chlorine (400 ppm)	70.92	2.69	3.53
Bromine (50 ppm)	94.46	2.19	3.23
Bromine (50 ppm)+ Chlorine (100 ppm)	96.68	2.09	2.33
Bromine (50 ppm)+ Chlorine (400 ppm)	97.68	2.33	4.54

Mercury Oxidation under Oxy-Fuel Conditions

Table C.6. Effect of chlorine and the high and low quench temperature profiles.

Conditions	% Hg Oxidation (average)	Error bars	
		Minimum	Maximum
100 ppm Cl-HQ	69.54	2.35	1.56
100 ppm Cl-LQ	71.12	1.38	0.86
400 ppm Cl-HQ	74.47	1.02	3.63
400 ppm Cl-LQ	80.72	0.72	0.49

Table C.7. Effect of bromine and the high and low quench temperature profiles.

Conditions	% Hg Oxidation (average)	Error bars	
		Minimum	Maximum
25 ppm Br-HQ	74.35	2.05	1.87
25 ppm Br-LQ	89.34	3.58	1.4
50 ppm Br-HQ	98.7	0.76	1.05
50 ppm Br-LQ	97.95	0.87	0.76